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PART II

Amino acid Content of the Seed of *Moringa concanensis*

By

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Abstract

The seed of the plant *Moringa concanensis* has been subjected to chemical investigation with a view to determine its amino acid content. The isolated proteins were found to be made up of arginine, serine, histidine, valine, proline, hydroxyproline, threonine, alanine, phenylalanine and leucine.

Introduction

The *Moringaceae* family is a small family with only three species, viz., *M. oleifera*, *M. concanensis* and *M. aptera*, which are indigenous to Arabia, India and Syria. In India, these species are widely distributed in Rajputana, dry hills of Konkan, Deccan, Kurnool and Coimbatore. *M. oleifera* and *M. concanensis* have similar medicinal properties and the medicinal use of different parts of the plant i.e., root, bark, fruits, flowers and seeds, has been described.^{1,2} The seeds are used in venereal affections and the oil from seeds is used as external application in rheumatism. The oil is stated to be unusually resistant to the development of rancidity, and is recommended as suitable for enflourage and as a lubricant for precision machineries and watches. In view of the medicinal importance of the plant, it was thought of interest to subject the seeds of *Moringa concanensis* to a systematic chemical examination. In the present communication, the authors describe the isolation of proteins from the seeds and the characterization of amino acids in the protein hydrolysates by descending paper chromatographic technique.

Procedure and results

No single solvent has, so far, been found suitable to isolate completely the protein matter from plants and seeds. Water, neutral saline solution, 70-80% alcohol and dilute solutions of acids and alkalis have been commonly employed by earlier workers^{3,4} to isolate proteins from plants. The complete isolation of protein matter from the seed of *M. concanensis* was achieved by employing water, 10% NaCl and 0.25% NaOH solutions as successive solvents.

(a) *Isolation of Protein matter from the seeds of M. concanensis*

The finely powdered seeds were extracted with Petroleum ether (40°-60°) in a Soxhlet extractor to remove the oil. The defatted seed powder (50 gm) was mixed with 500 ml of distilled water and stirred for about two hours and then filtered. The filtrate (No. 1) contained the water soluble proteins, and the residual seed powder still containing nitrogen was taken in 400 ml of 10% NaCl solution, stirred for about two hours and filtered. The filtrate (No. 2) contained the proteins soluble in NaCl solution. The residue still showed the presence of nitrogen, and was washed several times with distilled water to free it from NaCl. The washed seed powder was then shaken with 0.25% NaOH solution for two hours with constant stirring and finally filtered. The filtrate (No. 3) contained the NaOH soluble proteins and the residue was freed from NaOH by washing with distilled water. This residual seed powder did not give positive test for the presence of nitrogen showing that all the protein matter of the seed had completely been extracted by the above three solvents, viz., water, 10% NaCl and 0.25% NaOH solution.

(b) *Purification of Protein matter*

The filtrates (No. 1, 2 and 3) were treated separately in a desalting apparatus and then evaporated to dryness over a water bath. The protein matter obtained in the form of solid residue from the above filtrates weighed 2.23, 1.64 and 0.85 gm respectively.

(c) *Hydrolysis of the Protein matter*

About 0.5 gm of the protein matter from each filtrate was separately refluxed with 6N HCl for ten hours on a sand bath and then filtered. The hydrolysates were treated with NaOH solution to remove HCl and filtered. The filtrate was finally purified by desalting it in a desalting apparatus. Each of the hydrolysate was concentrated to a semi-solid mass and then extracted with ethanol.

(d) *Characterization of Amino acids*

The technique of paper chromatography has helped enormously in the isolation and characterization of amino acids. The amino acids present in the protein hydrolysates of the seed of *Moringa concanensis* were characterised by employing paper chromatographic technique.

(I) *Paper chromatography of protein hydrolysates*

Amino acids were identified by employing two dimensional descending paper chromatographic technique⁶. The hydrolysates together with reference amino acids were chromatographed on different sheets (44 × 26 cms.) of Whatman filter paper No. 1. The chromatograms were equilibrated with the lower layer of *n*-butanol-acetic acid-water mixture (4:1:5, v/v) for 24 hours and were then developed along one axis of the paper by the solvent phase (upper layer) of the above B.A.W. mixture for 36 hours at room temperature. The developed chromatograms were dried in air and were again developed in the same solvent along the other axis in order to achieve better and distinct separation. The developed chromatograms were sprayed with 0.1% solution of ninhydrin in acetone and the spots were located by placing them in an electric oven at 60° for fifteen minutes.

The amino acids identified in the protein hydrolysates obtained from the seed of *M. concanensis* are recorded in Table I :

TABLE I

Amino acids present in the protein hydrolysates of the seed of M. concanensis

Protein hydrolysate	Amino acids identified
1. Water soluble protein	Arginine, Serine, Valine, Proline, Leucine, Threonine, Alanine and Phenylalanine.
2. 10% NaCl soluble protein	Arginine, Serine, Valine, Hydroxyproline, Alanine, Phenylalanine and Leucine.
3. 0.25% NaOH soluble protein	Histidine, Serine, Valine, Leucine and Alanine.

(II) *Paper Chromatography of mixed Protein hydrolysates*

The three different hydrolysates were mixed thoroughly and the solution so obtained was chromatographed together with reference amino acids in the same way as described before. The chromatographic analysis showed the presence of all the amino acids described in Table 1.

From the above observations it is concluded that the proteins of the seeds of *M. concanensis* are built up of arginine, histidine, serine, valine, alanine, leucine, proline, hydroxyproline, threonine and phenylalanine.

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A theorem on Laplace transform

By

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Abstract

In this paper we have proved a theorem which is the generalisation of the Parseval Goldstein theorem in the theory of Laplace Transform. Theorems obtained by me, Gupta, Rathie, Saxena, Varma and Shastri have been shown as particular cases of the theorem. Later on Weyl Fractional integrals involving F_4 and H-function have been evaluated with the help of the theorem.

Introduction

The object of this paper is to enunciate and prove a theorem on well known Laplace Transform defined by

$$\phi(p) = \int_0^\infty e^{-pt} f(t) dt \quad (1)$$

which is the generalisation of the well known Parseval Goldstein theorem [3, p. 105] in the theory of Laplace Transform.

Theorem gives us a new approach in finding the Weyl (Fractional) integral of the Appell's Hypergeometric function F_4 and H-function defined by Fox [2, p. 408].

Recently few theorems obtained by me and Gupta follows as corollaries of the theorem by specialising the functions $f(t)$ and $h(t)$. Later on more well known theorems given by Varma (1961), Saxena (1960, 1962), Rathie (1953, 1954) and Shastri (1945) have been shown as particular cases of the theorem.

Throughout this paper (1) shall be denoted symbolically as

$$\phi(p) \doteq f(t)$$

Theorem 1

If

$$\psi(p) \doteq f(t) \quad (2.1)$$

and

$$g(p) \doteq h(t) \quad (2.2)$$

then

$$\int_0^\infty e^{-pt} t^n g(t) f(t) dt = \int_p^\infty \psi(t) h^n(t-p) dt \quad (2.3)$$

$$= \int_0^\infty \psi(p+x) h^n(x) dx \quad (2.4)$$

provided that $f(t) \in L^2(0, \infty)$, $e^{-pt} t^n g(t) \in L^2(0, \infty)$ and $h^n(t)$ denotes the n^{th} differential coefficient of $h(t)$ such that $h'(0) = h''(0) = \dots = h^{n-1}(0) = 0$.

Proof

Applying well known property of Laplace Transform [1, p. 129].
that if

$$g(p) \doteq h(t)$$

then

$$p^n g(p) \doteq h^n(t)$$

provided that $h'(0) = h''(0) = \dots = h^{n-1}(0) = 0$

and

$$e^{-ap} g(p) \doteq h(t-a) H(t-a)$$

where $H(t)$ is Heaviside's Unit function.

We have

$$e^{-ap} p^n g(p) \doteq h^n(t-a) H(t-a) \quad (2.5)$$

Using (2.1) and (2.5) in the Parseval Goldstein theorem, which states that

if $\phi_1(p) \doteq h_1(t)$ and $\phi_2(p) \doteq h_2(t)$

then

$$\int_0^\infty \phi_1(t) h_2(t) dt = \int_0^\infty \phi_2(t) h_1(t) dt$$

we get

$$\int_0^\infty e^{-at} t^n g(t) f(t) dt = \int_0^\infty \psi(t) h^n(t-a) H(t-a) dt \quad (2.6)$$

Replacing a by p , we get

$$\begin{aligned} \int_0^\infty e^{-pt} t^n g(t) f(t) dt &= \int_p^\infty \psi(t) h^n(t-p) dt \\ &= \int_0^\infty \psi(p+x) h^n(x) dx \end{aligned}$$

which gives us the required result.

Corollary

On taking $a = 0$ and $n = 0$ in the (2.6), the theorem reduces to well known Parseval Goldstein theorem in the theory of Laplace Transform [3, p. 105].

Lemma I

If

$$g(p) \doteq h(t)$$

then

$$t^{n+l} H \begin{matrix} m, s \\ p, q \end{matrix} \left[zt^k \left| \begin{matrix} (a_1, e_1), \dots, (a_p, e_p) \\ (b_1, f_1), \dots, (b_q, f_q) \end{matrix} \right. \right] g(t)$$

$$\doteq 2^{l-1} \int_0^\infty t^{i-1} H_{p+2, q}^{m, s+2} \left[z (2/t)^k \left| \begin{matrix} (-l/2, k/2), (\frac{1}{2}-l/2, k/2), (a_1, e_1), \dots (a_p, e_p) \\ (b_1, f_1), \dots (b_q, f_q) \end{matrix} \right. \right] \times h^n(t-p) dt \quad (2.7)$$

where $h^n(t)$ denotes the n^{th} differential coefficient of $h(t)$ such that $h'(0) = h'(0) = \dots = h^{n-1}(0) = 0$; $k > 0$, $Re(p) > 0$, $Re(l + \frac{3}{2} \pm \frac{1}{2} + k \min b_h/f_h) > 0$, ($h = 1, \dots, m$), $h(t) \in L(0, \infty)$ and one of the following sets of condition is satisfied.

$$(i) \quad \lambda > 0, |\arg z| < \frac{1}{2} \lambda \pi.$$

$$(ii) \quad \lambda \geq 0, |\arg z| \leq \frac{1}{2} \lambda \pi, Re(\mu + l + 3/2) < 0, Re(\mu + 1) < 0$$

where

$$\lambda = \sum_{j=1}^s (e_j) - \sum_{j=r+1}^p (e_j) + \sum_{j=1}^m (f_j) - \sum_{j=m+1}^q (f_j)$$

$$\mu = \frac{1}{2} (p - q) + \sum_{j=1}^q (b_j) - \sum_{j=1}^p (a_j)$$

Proof

Since we have [4, p. 99]

$$f(t) = t^l H_{p, q}^{m, s} \left[z t^k \left| \begin{matrix} (a_1, e_1), \dots (a_p, e_p) \\ (b_1, f_1), \dots (b_q, f_q) \end{matrix} \right. \right]$$

$$\doteq 2^{l-1} d^{i-1} H_{p+2, q}^{m, s+2} \left[z 2/p)^k \left| \begin{matrix} (-l/2, k/2), (\frac{1}{2}-l/2, k/2), (a_1, e_1), \dots \\ (b_1, f_1), \dots \end{matrix} \right. \right] \times \frac{(a_p, e_p)}{(b_q, f_q)} \Bigg] = \psi(p)$$

$$k > 0, Re p > 0, Re(l + 3/2 \pm \frac{1}{2} + k \min b_h/f_h) > 0, h = 1, \dots, m$$

and one of the above sets of condition is satisfied, then substituting this value of $f(t)$ in (2.3), we get (2.7).

Lemma II

If

$$g(p) \doteq h(t)$$

then

$$t^{n+k-3/2} J_\rho(at) I_\sigma(bt) g(t) \doteq \frac{2^{k-2} a^\rho b^\sigma \Gamma_{\frac{1}{2}}(k + \sigma + \rho \pm \frac{1}{2})}{\Gamma(1 + \rho) \Gamma(1 + \sigma)}$$

$$\int_p^\infty t^{k-\rho-\sigma+1} F_4 \left[\frac{1}{2}(k + \sigma + \rho - \frac{1}{2}), \frac{1}{2}(k + \sigma + \rho + \frac{1}{2}); 1 + \rho, 1 + \sigma, -\frac{a^2}{t^2}, \frac{b^2}{t^2} \right] h^n(t-p) dt \quad (2.8)$$

where $h^{(n)}(t)$ denotes the n^{th} differential coefficient of $h(t)$, such that $h'(0) = h''(0) = \dots = h^{(n-1)}(0) = 0$, $Re(k + \sigma + \rho \pm \frac{1}{2}) > 0$, $Re(p - b) > 0$, $a > 0$ and $h(t) \in L(0, \infty)$.

Proof

If we take $f(t) = t^{k-3/2} J_\rho(at) I_\sigma(bt)$, then [12, p. 110]

$$\begin{aligned} f(t) &= t^{k-3/2} J_\rho(at) I_\sigma(bt) \\ &\doteq 2^{k-2} \frac{a^\rho b^\sigma \Gamma(\frac{1}{2}k + \sigma + \rho \pm \frac{1}{2})}{\Gamma(1 + \rho) \Gamma(1 + \sigma)} p^{-k-\rho-\sigma+\frac{1}{2}} \\ &\times F_4 \left[\frac{1}{2}(k + \rho + \sigma - \frac{1}{2}), \frac{1}{2}(k + \rho + \sigma + \frac{1}{2}); 1 + \rho, 1 + \sigma; -a^2/p^2, b^2/p^2 \right] = \psi(p) \end{aligned}$$

$$Re(k + \sigma + \rho \pm \frac{1}{2}) > 0, Re(p - b) > 0, a > 0,$$

substituting this value of $f(t)$ in (2.3), we get (2.8).

Example I

On taking $h(t) = t^v$ then [1, p. 137]

$$h(t) = t^v \doteq \Gamma(v+1) p^{-v-1} = g(p), \quad Re(v) > -1, Re(p) > 0$$

so that we have

$$h^{(n)}(t) \equiv \frac{\Gamma(v+1)}{\Gamma(v-n+1)} t^{v-n} \quad \text{where } h'(0) = h''(0) = \dots = h^{(n-1)}(0) = 0 \text{ if } v > n-1$$

substituting this value in the relation (2.7) and solving right hand side integral with the help of the result [4, p. 99],

we get

$$\begin{aligned} &\int_0^\infty t^{-l-1} (t-p)^{r-n} H_{p+2, q}^{m, s+2} \left[z \left(\frac{2}{t} \right)^k \left| \begin{matrix} (-l/2, k/2), (\frac{1}{2}-l/2, k/2), (a_1, e_1), \dots, (a_p, e_p) \\ (b_1, f_1), \dots, (b_q, f_q) \end{matrix} \right. \right] dt \\ &= \sqrt{v-n+1} 2^{n-v-1} p^{r-l-n} H_{p+2, q}^{m, s+2} \left[z \left(\frac{2}{p} \right)^k \left| \begin{matrix} \left(\frac{v}{2} - \frac{l}{2} - \frac{n}{2} + \frac{1}{2}, \frac{k}{2} \right), \left(\frac{v}{2} - \frac{l}{2} - \frac{n}{2} + 1, \frac{k}{2} \right) \\ (b_1, f_1), \dots, (b_q, f_q) \end{matrix} \right. \right. \\ &\quad \left. \left. \begin{matrix} (a_1, e_1), \dots, (a_p, e_p) \\ (b_q, f_q) \end{matrix} \right] \right] \end{aligned}$$

$$k > 0, Re(p) > 0, Re \left(l + n - v + \frac{1}{2} \pm \frac{1}{2} + k \min \frac{b_h}{f_h} \right) > 0 \quad (2.9)$$

$$h = 1, \dots, m, v > n-1$$

and one of the above sets of conditions (i) or (ii) is satisfied, (2.9) gives us a new approach in finding the Weyl (Fractional) integral of H-function.

Now taking $k = 2$, $e^t s$ and $f^t s$ equal to unity in (2.9) and applying the relation [4, p. 99]

$$H_{p, q}^{m, n} \left[x \left| \begin{matrix} (a_1, s), \dots, (a_p, s) \\ (b_1, s), \dots, (b_q, s) \end{matrix} \right. \right] = \frac{1}{s} G_{p, q}^{m, n} \left[x^{1/s} \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right]$$

where s is a positive integer.

We get Weyl (Fractional) integral for G-function.

$$\begin{aligned} & \int_p^\infty t^{-l-1} (t-p)^{v-n} G_{p+2, q}^{m, s+2} \left[\frac{4z}{t^2} \left| \begin{matrix} -l/2, \frac{1}{2} - l/2, a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right] dt \\ &= \Gamma(v-n+1) 2^{n-l-1} p^{l-n} G_{p+2, q}^{m, s+2} \left[\frac{4z}{p^2} \left| \begin{matrix} \frac{v}{2} - \frac{l}{2} - \frac{n}{2} + \frac{1}{2}, \frac{v}{2} - \frac{l}{2} - \frac{n}{2} + 1, a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right] \\ & \quad v > n-1, \operatorname{Re}(p) > 0, \operatorname{Re}(l+n-v+\frac{1}{2} \pm \frac{1}{2} + 2 \min b_h) > 0 \quad (2.10) \\ & \quad h = 1, \dots, m. \end{aligned}$$

Example II

On taking [1, p. 137]

$$h(t) = t^v = \sqrt{v+1} p^{v-1} = g(p), \operatorname{Re}(v) > -1, \operatorname{Re}(p) > 0,$$

so that

$$h^n(t) \equiv \frac{\Gamma(v+1)}{\Gamma(v+n+1)} t^{v-n} \text{ where } h'(0) = h''(0) = \dots = h^{n-1}(0) = 0, \text{ if } v > n-1$$

substituting these values in the relation (2.8) and solving right hand side integral with the help of the result [12, p. 110], we get

$$\begin{aligned} & \int_p^\infty t^{-k-\rho-\sigma+\frac{1}{2}} (t-p)^{v-n} F_4 \left[\begin{matrix} \frac{1}{2}(k+\sigma+\rho-\frac{1}{2}), \frac{1}{2}(k+\sigma+\rho+\frac{1}{2}) \\ 1+\rho, 1+\sigma \end{matrix} ; -\frac{a^2}{t^2}, \frac{b^2}{t^2} \right] dt \\ &= 2^{n-l-1} \frac{\Gamma(v-n+1) \Gamma(\frac{1}{2}(k+n+\sigma+\rho-\frac{1}{2}-v)) \Gamma(\frac{1}{2}(k+n+v+\sigma+\rho-3/2))}{\Gamma(\frac{1}{2}\{(k+\sigma+\rho+\frac{1}{2})\}) \Gamma(\frac{1}{2}\{(k+\sigma+\rho-\frac{1}{2})\})} p^{v-n-k-\rho-\sigma+3/2} \\ & \quad F_4 \left[\begin{matrix} \frac{1}{2}(n+k-v+p+\sigma-3/2), \frac{1}{2}(k+n-v+\sigma+\rho-\frac{1}{2}) \\ 1+\rho, 1+\sigma \end{matrix} ; -\frac{a^2}{p^2}, \frac{b^2}{p^2} \right] \\ & \quad \operatorname{Re}(k+n-v-1 \pm \frac{1}{2} + \sigma + \rho) > 0, \operatorname{Re}(p-b) > 0, a > 0 \quad (2.11) \\ & \quad v > n-1. \end{aligned}$$

(2.11) gives us Weyl (Fractional) integral for the Appell's Hypergeometric function F_4 .

3. The above theorem I gives us as particular cases the following theorems by specialising the functions $f(t)$ and $h(t)$.

If we take $h(t) = t^\lambda e^{-\mu t}$ in the theorem I we obtain the following theorem recently given by me?

Theorem (1.1)

If

$$\psi(p) \doteq f(t)$$

then

$$t^n (t+a)^{-\lambda-1} f(t) \doteq \sum_{r=0}^n n_{c,r} \frac{(-1)^{n-r} a^{n-r}}{\Gamma(\lambda-r+1)} \int_0^\infty x^{\lambda-r} e^{-ax} \psi(p+x) dx \quad (3.1)$$

provided that Laplace Transform of $|f(t)|$ exist, $\lambda > n-1$, $Re(p+a) > 0$ and the integral (3.1) is absolutely convergent.

When we take $f(t) = t^{n-1}$ in the theorem I, we obtain

Theorem (1.2)

If

$$g(p) \doteq h(t)$$

and

$$\phi(p) \doteq t^{n+v-1} g(t)$$

then

$$\phi(p) = \Gamma v \int_0^\infty (p+x)^{-v} h^n(x) dx \quad (3.2)$$

provided that $Re(v) > 0$, $Re(p) > 0$, Laplace Transform of $|h(t)|$, $|t^{n+v-1} g(t)|$ exist, $h^n(t)$ denotes the n^{th} differential coefficient of $h(t)$ such that $h'(0) = h''(0) = \dots = h^{n-1}(0) = 0$ and the integral (3.2) is absolutely convergent.

When we take $h(t) = t_v(at)$ in theorem I, we obtain

Theorem (1.3)

If

$$\psi(p) \doteq f(t)$$

then

$$a^{n-v} \left(\frac{1}{2}\right)^n \sum_{r=0}^n n_{c,r} \int_0^\infty I_{v+2r-n}(at) \psi(t+p) dt \doteq t^n (t^2 - a^2)^{-\frac{1}{2}} (t + \sqrt{t^2 - a^2})^{-v} f(t) \quad (3.3)$$

provided that $Re(v) > -1$, $Re(p) > Re(a)$, Laplace Transform of $|f(t)|$ exist and the integral (3.3) is absolutely convergent.

On the other hand if we take $n = 0$, we get the following theorem given earlier by Gupta [5, p. 245].

Theorem (1.4).

If

$$\psi(p) \doteq f(t)$$

$$g(p) \doteq h(t)$$

and

$$\phi(p) \doteq g(t) f(t)$$

then

$$\phi(p) = \int_0^\infty \psi(t) h(t-p) dt \quad (3.4)$$

$$= \int_0^\infty \psi(p+x) h(x) dx \quad (3.5)$$

provided that Laplace Transform of $|f(t)|$, $|h(t)|$ and $|g(t) \cdot f(t)|$ exist and the integral (3.4) and (3.5) are absolutely convergent.

The theorem (1.4) is quite general and include as particular cases some well known theorems as given below.

- (i) If we take $g(t) = (t+a)^{-\nu} (t+b)^{-\eta}$ then above theorem reduces in a theorem given by Saxena (1962, p. 183).
- (ii) On taking $f(t) = t^{v-1} e^{-at^2}$ theorem (1.4) gives us a theorem given by Rathie (1953, p. 136).
- (iii) On taking $f(t) = t^{2v-1} e^{-at}$ it takes the form which was given as theorem by Rathie (1954, p. 62).
- (iv) On taking $f(t) = t^m (1+t)^l$ in the above theorem (1.4) it gives a theorem given by Shastri (1945, p. 4).
- (v) On taking in the above theorem $f(t) = t^{v-1} \exp(-at^{n/s})$ we get again a theorem given by Saxena (1961, p. 43).
- (vi) If we take in the above theorem (1.4), $f(t) = t^{v-1} \exp(-at^{n/s})$ we get a theorem given by Saxena (1961, p. 49).
- (vii) If we take $f(t) = t^{v-1} (1+t^{n/s})^{-\alpha}$, we get again a theorem given by Saxena (1961, p. 55).
- (viii) On the other hand if we take $g(t) = (1-t)^n t^{-m-n-1}$ and $f(t) = (1-t)^{-\alpha} t^{\beta-1}$ the above theorem reduces to a corresponding result obtained by Varma (1961, p. 190).

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Kinetics and Mechanism of the reaction between Bromine and Iso-Quinoline in Carbon Tetrachloride Solution

By

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Abstract

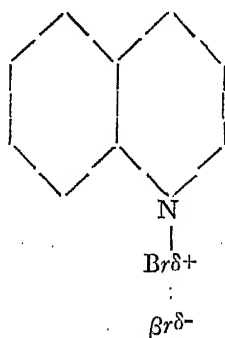
In the reaction between bromine and iso-quinoline in carbon-tetrachloride, the total order of the reaction is two, one with respect to each of the reactants. The second order constants are calculated from the initial rate ($-\frac{dc}{dt}$), which is obtained by drawing graphs between concentration against time. The rate equation has been derived as

$$-\frac{d[Br_2]}{dt} = 2k_1 [\text{Iso-quinoline}] [\text{Bromine}]$$

where $2k_1$ is equal to k (second order constant).

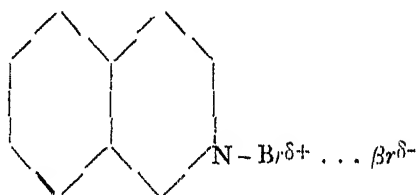
Introduction

In the present work kinetics of the reaction between bromine and iso-quinoline has been studied using carbon-tetrachloride as solvent, for the first time. The exact nature of the reaction product, when bromine reacts with pyridine, quinoline and acridine in carbon-tetrachloride at ordinary temperature has been discussed in detail by Williams¹ (He prepared the compound $C_5H_5NBr_2$ in carbon-tetrachloride and suggested that it is an addition product), Acheson, Hoult and Barnard² (prepared the addition product of acridine in carbon-tetrachloride) and more recently by Eisch³ (He prepared the complex $C_9H_7NBr_2$ by interaction of quinoline and bromine in inert solvents and has studied the properties of the complex as thermal and photochemical decomposition, spectral studies and the infrared spectrum of the solid complex). Eisch's work indicates that quinoline forms an addition product with bromine in carbon-tetrachloride. The structural formula which has been ascribed to this addition product is as follows :



quinoline dibromide.

Similarly isoquinoline also forms addition product¹ with bromine in carbon-tetrachloride. The following structural formula has been postulated.



isoquinoline di-bromide

The above structural formula is also valid from equivalents (one mole of isoquinoline required one mole of bromine). This compound is stable in carbon-tetrachloride and isoquinoline but gradually decomposes in ionising solvents like water and alcohol. Since we have performed kinetic measurements in carbon-tetrachloride as solvent, the reaction product remains stable throughout entire course of the reaction.

The reaction between bromine and isoquinoline in carbon-tetrachloride proceeds very fast and a (rapid) precipitation of isoquinoline di-bromide occurs. In such reactions, therefore, we have taken into consideration the initial rate obtained by drawing graphs between concentration against time and these indicate that reaction is initially of second order (The order being one both with respect to bromine and isoquinoline) at all temperatures.

Experimental

The reaction bottle (blackened with japan black from outside and covered with black cloth) containing adjustable quantities of bromine and carbon-tetrachloride was kept in a thermostat ($\pm 0.1^\circ\text{C}$). Isoquinoline was kept in a separate conical flask, when the reactants had attained the temperature of the bath, the requisite quantity of isoquinoline was sucked through a pipette and poured into the reaction bottle. The stop watch was started as soon as half of isoquinoline had passed out of the pipette. An aliquot (5 ml.) of the reaction mixture was withdrawn (through glass wool put at the nozzle of the pipette with the help of a suitable device) from the reaction bottle at scheduled intervals and poured into 10 ml. of 15% potassium iodide solution. This immediately 'quenches' the reaction and liberated iodine^{5,6} was titrated by a standard solution of sodium thiosulphate (hypo), using starch as an indicator and with the help of micro-burette. All the materials (required for the reaction and titration) were either A. R. (B. D. H.) or G. R. (E. Merck) grade samples.

Results and Discussion

Determination of the Total order of Reaction between Bromine and Isoquinoline

It has been observed that total order of the reaction is two. One with respect to each of the reactants and since the reaction becomes heterogeneous due to precipitation of the reaction product, it is quite likely that some of the bromine might be adsorbed and hence, only the initial slopes (*i.e.* upto the point where one third or one half of the reaction is over) have been taken for calculating the

second order constants. Although the corresponding table show the progress of the reaction to about 80% to 90% of the reaction. The initial rate of disappearance of bromine can be given as :

$$-\frac{d[Br_2]}{dt} = k [\text{Isoquinoline}] [\text{Bromine}]$$

where k is the second order constant. It is found that Equation (1) holds good in all cases and all temperatures. The value of k is determined by determining the value of $(-\frac{dc}{dt})$, which is obtained by plotting graphs (see fig. 1) between concentration against time. The slope (*i.e.* dc/dt) is determined by drawing tangent at the initial part of the reaction (shown by arrow in Fig. I, curve I, II and III).

The following summarized tables (I and II) show the study of the reaction at different temperatures and concentrations of Isoquinoline and bromine.

TABLE I
Effect of variation of isoquinoline concentration

$[\text{Bromine}]_0 = 15.52 \times 10^{-3} \text{ M}$

Temp. °C	[Isoquinoline] ₀ × 10 ²	[Bromine]* × 10 ³	$(-\frac{dc}{dt}/2)$ mole per min.	$k \times 10$ litres mole ⁻¹ min ⁻¹
30	10.14M	10.99 M	4.66	38.78
	13.53M	9.26 M	5.00	38.96
	20.29M	9.26 M	7.00	34.49
	27.08M	7.06 M	4.16	32.31 ± 6.3%
35	6.765M	13.19 M	2.66	27.68
	8.455M	14.00 M	3.00	23.46
	10.14 M	12.73 M	3.00	21.52
	13.53 M	11.53 M	4.00	23.67
	16.91 M	11.68 M	5.25	24.84
	20.29 M	10.23 M	5.00	21.91 ± 6.73%
40	10.14 M	11.47 M	4.33	34.12
	13.53 M	11.47 M	5.50	32.53
	20.29 M	9.745M	7.00	32.47
	27.06 M	8.025M	7.00	29.59 ± 4.03%
45	10.14 M	12.84 M	5.25	37.69
	13.53 M	10.51 M	6.25	41.08
	20.29 M	9.58 M	5.75	36.84
	27.06 M	8.64 M	9.66	38.61 ± 3.34%

TABLE II

Effect of variation of bromine concentration

$$[\text{Isoquinoline}]_0 = 16.91 \times 10^{-2} \text{M}$$

Temp. °C	[Bromine] ₀ × 10 ³	[Bromine]* × 10 ³	(- $\frac{dc}{dt}$ / 2) mole per unit	k × 10 litres mole ⁻¹ min ⁻¹
30	11.64 M	5.68 M	4.00	37.86
	19.40 M	12.96 M	4.33	37.30
	23.28 M	15.32 M	4.50	32.76
	38.81 M	28.28 M	8.00	31.58 ± 7.75%
35	11.64 M	6.81 M	3.00	23.67
	13.58 M	9.345 M	4.33	25.64
	19.40 M	13.32 M	2.50	21.13
	23.28 M	19.03 M	4.50	26.63
	27.16 M	20.46 M	4.00	22.02
	31.05 M	22.92 M	2.25	21.29 ± 8.16%
40	11.64 M	6.535 M	4.50	37.27
	19.40 M	14.14 M	4.66	36.83
	23.28 M	17.21 M	5.00	32.42 ± 5.8%
45	19.40 M	15.32 M	5.00	36.41
	23.28 M	18.85 M	6.00	35.50 ± 1.26%

Here [Bromine]₀ represents the initial concentration of bromine.

[Bromine]* represents the concentration of bromine at which the slope is actually measured.

[Isoquinoline]₀ represents the initial concentration of isoquinoline.

$$\text{and } k = \frac{(-\frac{dc}{dt}/2) \times S/V}{[\text{Bromine}]^* [\text{Isoquinoline}]_0}$$

In this equation the quantity $(-\frac{dc}{dt}/2)$ represents the slope in terms of molar concentration of bromine.

$(-\frac{dc}{dt}) \times S/V$ represents the change in gm. molar concentration of bromine

per minute per litre of the solution. Where S is the strength of the hypo used in the estimation and V , the volume of the aliquot taken. In the last the quantity

$$\frac{\left(-\frac{dc}{dt}/2\right) \times S/V}{[\text{Bromine}]^* [\text{Isoquinoline}]_0}$$

gives the value of the second order constant in terms of litres mole⁻¹ min.⁻¹

A perusal of the above tables (I and II) shows that the value of k is practically constant showing the validity of the equation (1).

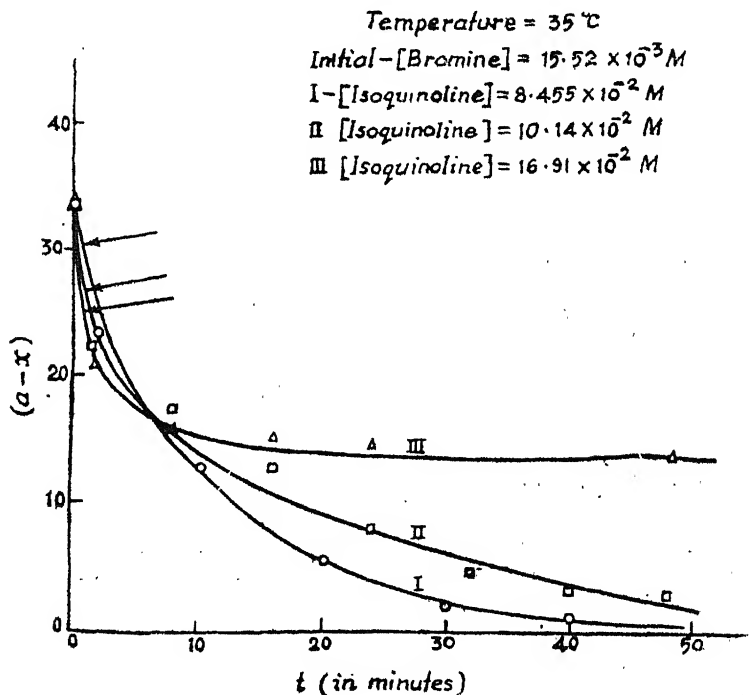
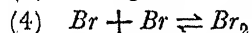
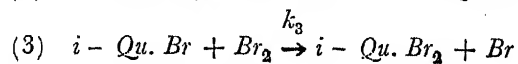
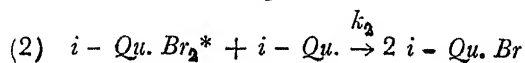
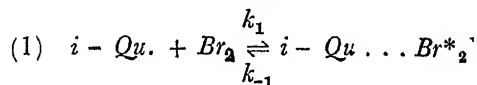


Fig. 1

Mechanism

We propose the following steps during the reaction between bromine and isoquinoline and in carbon-tetrachloride.



where $i - Qu.$ represents the isoquinoline.

The compound $i\text{-}Qu \dots Br_2^*$ may be regarded as activated complex in which the atoms have not, yet, been organized into a normal molecule, obviously the rate of variation of concentration is given by the expression.

$$-\frac{d[Br_2]}{dt} = k_1 [i - Qu] [Br_2] + k_3 [i - Qu. Br] [Br_2] - k_{-1} [i - Qu. Br_2^*] \quad (2)$$

from the principle of stationary state, at stationary state we have

$$\frac{d[i - Qu \dots Br_2^*]}{dt} = k_1 [i - Qu.] [Br_2] - k_{-1} [i - Qu. Br_2^*] - k_2 [i - Qu. Br_2^*] [i - Qu.] = 0$$

$$\text{or} \quad [i - Qu. \dots Br_2^*] = \frac{k_1 [i - Qu.] [Br_2]}{k_{-1} + k_2 [i - Qu.]} \quad (3)$$

also

$$\frac{d[i - Qu. Br]}{dt} = k_2 [i - Qu. \dots Br_2^*] [i - Qu.] - k_3 [i - Qu. Br] [Br_2] = 0$$

$$\text{or} \quad [i - Qu. Br] = \frac{k_2 [i - Qu. \dots Br_2^*] [i - Qu.]}{k_3 [Br_2]} \quad (4)$$

Comparing equations (2), (3) and (4) we have

$$-\frac{d[Br_2]}{dt} = \frac{2k_1 k_2 [i - Qu.]^2 [Br_2]}{k_{-1} + k_2 [i - Qu.]} \quad (5)$$

In the reaction between bromine and isoquinoline the concentration of isoquinoline has always been kept much higher than that of bromine. Under these condition $k_2 [i - Qu.] \gg k_{-1}$ and equation (5) reduces to

$$-\frac{d[Br_2]}{dt} = 2k_1 [i - Qu] [Br_2] \quad (6)$$

which is a simple second order expression as has been confirmed by the measurement of the constants in the initial part of the reaction. The value of k in tables (I and II) is equal to $2k_1$ in the expression (6).

A perusal of the tables (I and II) shows that the value of the second order constant between 30°C at 45°C at first decrease and then increases with the rise in temperature. This is obviously due to the different rate of variation with temperature in the values of k_1 , k_{-1} , k_2 and k_3 etc.

The mechanism put forward by us for the reaction between bromine and isoquinoline, therefore adequately explain the present kinetic data.

Acknowledgment

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Integrals involving generalised Function of two variables (II)

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Abstract

In this paper we evaluate some integrals involving generalised function of two variables. The results are of general character and in particular we obtain some integrals involving the product of Meijer's G-function.

1. Introduction

In a recent paper [7] the author has defined the generalised function of two variables as follows

$$\left[\begin{matrix} \left[\begin{matrix} m_1, 0 \\ p_1-m_1, q_1 \end{matrix} \right] \\ \left(\begin{matrix} m_2, n_2 \\ p_2-m_2, q_2-n_2 \end{matrix} \right) \\ \left(\begin{matrix} m_3, n_3 \\ p_3-m_3, q_3-n_3 \end{matrix} \right) \end{matrix} \middle| \begin{matrix} a_1, \dots, a_{p_1}; b_1, \dots, b_{q_1} \\ c_1, \dots, c_{p_2}; d_1, \dots, d_{q_2} \\ e_1, \dots, e_{p_3}; f_1, \dots, f_{q_3} \end{matrix} \right] x, y$$

$$= \frac{1}{(2\pi i)^2} \int_{L_1} \int_{L_2} \frac{\prod_{j=1}^{m_1} \Gamma(a_j+s+t) \prod_{j=1}^{m_2} \Gamma(1-c_j+s) \prod_{j=1}^{n_2} \Gamma(d_j-s)}{\prod_{j=m_1+1}^{p_1} \Gamma(1-a_j-s-t) \prod_{j=1}^{q_1} \Gamma(b_j+s+t) \prod_{j=m_2+1}^{q_2} \Gamma(c_j-s)}$$

$$\times \frac{\prod_{j=1}^{m_3} \Gamma(1-e_j+t) \prod_{j=1}^{n_3} \Gamma(f_j-t)}{\prod_{j=n_2+1}^{q_2} \Gamma(1-d_j+s) \prod_{j=m_3+1}^{p_3} \Gamma(e_j-t) \prod_{j=n_3+1}^{q_3} \Gamma(1-f_j+t)} x^s y^t ds dt, \quad (1)$$

where L_1 and L_2 are suitable contours and the positive integers $p_1, p_2, p_3, q_1, q_2, q_3, m_1, m_2, m_3, n_2$ and n_3 satisfy the following inequalities.

$q_2 \geq 1, q_3 \geq 1, p_1 \geq 0, q_1 \geq 0, 0 \leq m_1 \leq p_1, 0 \leq m_2 \leq p_2, 0 \leq n_2 \leq q_2, 0 \leq m_3 \leq p_3, 0 \leq n_3 \leq q_3, p_1 + p_2 \leq q_1 + q_2$ and $p_1 + p_3 \leq q_1 + q_3$.

The values $x = 0$ and $y = 0$ are excluded.

In other two papers [8, 9] the author has discussed the simple properties and particular cases of the generalised function. In my previous paper [10] I have evaluated an integral involving generalised function of two variables.

The object of this paper is to evaluate some integrals involving generalised function of two variables. The results are of general character and in particular we obtain some integrals involving the product of two G-functions.

In the proof we require the formula [2, p. 4]

$$\prod_{k=0}^{m-1} \Gamma\left(z + \frac{k}{m}\right) = (2\pi)^{\frac{1}{2}m-\frac{1}{2}} (m)^{\frac{1}{2}-mz} \Gamma(mz) \quad (2)$$

and the integrals [3, p. 331, equations (26) and (28)].

$$\int_0^\infty x^{\lambda-1} k_\nu(ax) dx = a^{-\lambda} 2^{\lambda-2} \Gamma(\tfrac{1}{2}\lambda \pm \tfrac{1}{2}\nu), \quad (3)$$

valid for $R(a) > 0$, $R(\lambda) > |R(\nu)|$.

$$\int_0^\infty x^{\lambda-1} e^{-ax} k_\nu(ax) dx = \frac{\sqrt{\pi} \Gamma(\lambda \pm \nu)}{2^\lambda a^\lambda \Gamma(\lambda + \tfrac{1}{2})} \quad (4)$$

valid for $R(a) > 0$, $R(\lambda) > |R(\nu)|$.

2. The first formula to be proved is

$$\begin{aligned} & \int_0^\infty x^{\lambda-1} k_\nu(ax) S \left[\begin{matrix} \left[\begin{matrix} 0, 0 \\ p_1, q_1 \end{matrix} \right] \\ \left(\begin{matrix} m_2, n_2 \\ p_2-m_2, q_2-n_2 \end{matrix} \right) \\ \left(\begin{matrix} m_3, n_3 \\ p_3-m_3, q_3-n_3 \end{matrix} \right) \end{matrix} \middle| \begin{matrix} a_1, \dots, a_{p_1}; b_1, \dots, b_{q_1} \\ c_1, \dots, c_{p_2}; d_1, \dots, d_{q_2} \\ e_1, \dots, e_{p_3}; f_1, \dots, f_{q_3} \end{matrix} \right] \beta x^{2n} x, \delta x^{2n} dx \\ &= \frac{(a)^{-\lambda} 2^{\lambda-n-2} (\pi)^{1-n}}{(n)^{1-\lambda}} S \left[\begin{matrix} \left[\begin{matrix} 2n, 0 \\ p_1, q_1 \end{matrix} \right] \\ \left(\begin{matrix} m_2, n_2 \\ p_2-m_2, q_2-n_2 \end{matrix} \right) \\ \left(\begin{matrix} m_3, n_3 \\ p_3-m_3, q_3-n_3 \end{matrix} \right) \end{matrix} \middle| \begin{matrix} A_1, \dots, A_n, B_1, \dots, B_n, a_1, \dots, a_{p_1}; \\ b_1, \dots, b_{q_1} \\ c_1, \dots, c_{p_2}; d_1, \dots, d_{q_2} \\ e_1, \dots, e_{p_3}; f_1, \dots, f_{q_3} \end{matrix} \right] \\ & \quad \left[\frac{(2n)^{2n} \beta}{a^{2n}}, \frac{(2n)^{2n} \delta}{a^{2n}} \right] \quad (5) \end{aligned}$$

where

$$A_k = \Gamma\left(\frac{\lambda+\nu+2k}{2n}\right), B_k = \Gamma\left(\frac{\lambda-\nu+2k}{2n}\right), k = 0, 1, \dots, (n-1),$$

$2(m_2 + n_2) > p_1 + p_2 + q_1 + q_2$, $2(m_3 + n_3) > p_1 + q_1 + p_3 + q_3$,
 $|\arg \beta| < (m_2 + n_2 - \frac{1}{2}p_1 - \frac{1}{2}q_1 - \frac{1}{2}p_2 - \frac{1}{2}q_2) \pi$, $|\arg \delta| < (m_3 + n_3 - \frac{1}{2}p_1 - \frac{1}{2}q_1 - \frac{1}{2}p_3 - \frac{1}{2}q_3) \pi$, $m_2 \geq 1$, $m_3 \geq 1$, $R(\lambda \pm v + 2n d_j + 2n f_k) > 0$, $j = 1, 2, \dots, n_2$,
 $k = 1, 2, \dots, n_3$, $R(\alpha) > 0$,

n is a positive integer.

To prove (5) we substitute the value of the generalised function of two variables from (1) in the integrand of (5) change the order of integration (which we suppose to be permissible) and make use of (3) to evaluate the inner integral then by virtue of (2), we have

$$\begin{aligned} & \frac{(\alpha)^{-\lambda} 2^{\lambda-n-1} (\pi)^{1-n}}{(n)^{1-\lambda}} \frac{1}{(2\pi i)^2} \int_{L_1} \int_{L_2} \frac{\prod_{j=1}^{m_2} \Gamma(1-c_j+s)}{\prod_{j=1}^{p_1} \Gamma(1-a_j-s-t) \prod_{j=1}^{q_1} \Gamma(b_j+s+t)} \times \\ & \frac{\prod_{j=1}^{n_2} \Gamma(d_j-s) \prod_{j=1}^{m_3} \Gamma(1-e_j+t) \prod_{j=1}^{n_3} \Gamma(f_j-t) \prod_{k=0}^{n-1} \Gamma(\frac{\lambda+v+2k}{2n}+s+t)}{\prod_{j=m_2+1}^{p_2} \Gamma(c_j-s) \prod_{j=n_2+1}^{q_2} \Gamma(1-d_j+s) \prod_{j=m_3+1}^{p_3} \Gamma(e_j-t) \prod_{j=n_3+1}^{q_3} \Gamma(1-f_j+t)} \times \\ & \prod_{k=0}^{n-1} \Gamma(\frac{\lambda-v+2k}{2n}+s+t) \left[\frac{\beta(2n)^{2n}}{(\alpha)^{2n}} \right]^s \left[\frac{\delta(2n)^{2n}}{(\alpha)^{2n}} \right]^t ds dt. \end{aligned} \quad (6)$$

The contour L_1 is in the s -plane and runs from $-i\infty$ to $+i\infty$ with loops, if necessary to ensure that the poles of $\Gamma(d_j-s)$, $j = 1, 2, \dots, n_2$ lie to the right of the contour and the poles of $\Gamma(1-c_j+s)$, $j = 1, 2, \dots, m_2$, $\Gamma(\frac{\lambda \pm v + 2k}{2n} + s + t)$, $k = 0, 1, \dots, (n-1)$ to the left of the contour.

Similarly the contour L_2 is in the t -plane and runs from $-i\infty$ to $+i\infty$ with loops, if necessary to ensure that the poles of $\Gamma(f_j-t)$, $j = 1, 2, \dots, n_3$ lie to the right of the contour and the poles of $\Gamma(1-e_j+t)$, $j = 1, 2, \dots, m_3$, $\Gamma(\frac{\lambda \pm v + 2k}{2n} + s + t)$, $k = 0, 1, \dots, (n-1)$ to the left of the contour.

On interpreting (6) with the help of (1), we get (5) under the conditions stated therein.

Particular cases

Taking $p_1 = q_1 = 0$ and using the formula (9)

$$S \left[\begin{array}{c} \left[\begin{array}{c} 0, 0 \\ 0, 0 \end{array} \right] \\ \left(\begin{array}{c} m_2, n_2 \\ p_2 - m_2, q_2 - n_2 \end{array} \right) \\ \left(\begin{array}{c} m_3, n_3 \\ p_3 - m_3, q_3 - n_3 \end{array} \right) \end{array} \right] \left[\begin{array}{c} ; \\ c_1, \dots, c_{p_2}; d_1, \dots, d_{q_2} \\ e_1, \dots, e_{p_3}; f_1, \dots, f_{q_3} \end{array} \right] \left[\begin{array}{c} x, y \end{array} \right] =$$

$$= G_{p_2, q_2}^{n_2, m_2} \left(x \left| \begin{matrix} c_1, \dots, c_{p_2} \\ d_1, \dots, d_{q_2} \end{matrix} \right. \right) G_{p_3, q_3}^{n_3, m_3} \left(y \left| \begin{matrix} e_1, \dots, e_{p_3} \\ f_1, \dots, f_{q_3} \end{matrix} \right. \right) \quad (7)$$

in (5), we get

$$\int_0^\infty x^{\lambda-1} k_\nu(\alpha x) G_{p_2, q_2}^{n_2, m_2} \left(\beta x^{2n} \left| \begin{matrix} c_1, \dots, c_{p_2} \\ d_1, \dots, d_{q_2} \end{matrix} \right. \right) G_{p_3, q_3}^{n_3, m_3} \left(\delta x^{2n} \left| \begin{matrix} e_1, \dots, e_{p_3} \\ f_1, \dots, f_{q_3} \end{matrix} \right. \right) dx$$

$$= \frac{2^{\lambda-n-1} (n)^{\lambda-1}}{(\pi)^{n-1} (\alpha)^{\lambda-1}} \left[\begin{matrix} \left[\begin{matrix} 2n, 0 \\ 0, 0 \end{matrix} \right] & \left| \begin{matrix} A_1, \dots, A_n, B_1, \dots, B_n; \\ c_1, \dots, c_{p_2}; d_1, \dots, d_{q_2} \end{matrix} \right. & \frac{\beta (2n)^{2n}}{(\alpha)^{2n}}, \frac{\delta (2n)^{2n}}{(\alpha)^{2n}} \\ \left(\begin{matrix} m_2, n_2 \\ p_2-m_2, q_2-n_2 \end{matrix} \right) & & \\ \left(\begin{matrix} m_3, n_3 \\ p_3-n_3, q_3-n_3 \end{matrix} \right) & \left| \begin{matrix} e_1, \dots, e_{p_3}; f_1, \dots, f_{q_3} \end{matrix} \right. & \end{matrix} \right] \quad (8)$$

where $A_k = \Gamma\left(\frac{\lambda+\nu+2k}{2n}\right)$, $B_k = \Gamma\left(\frac{\lambda-\nu+2k}{2n}\right)$, $k = 0, 1, \dots, (n-1)$.

$2(m_2+n_2) > p_2+q_2$, $2(m_3+n_3) > p_3+q_3$, $|\arg \beta| < (m_2+n_2-\frac{1}{2}p_2-\frac{1}{2}q_2)\pi$, $|\arg \delta| < (m_3+n_3-\frac{1}{2}p_3-\frac{1}{2}q_3)\pi$, $R(\lambda \pm \nu + 2n d_j + 2n f_h) > 0$, $j = 1, 2, \dots, n_2$, $h = 1, 2, \dots, n_3$, $R(\alpha) > 0$, n is a positive integer.

Taking $m_2 = 0$, $p_2 = 0$, $n_2 = q_2 = 2$, $d_1 = \frac{1}{2}\rho$, $d_2 = -\frac{1}{2}\rho$ and using the formula [2]

$$G_{02}^{20} \left(\frac{x^2}{4} \left| \begin{matrix} \frac{1}{2}\rho, -\frac{1}{2}\rho \end{matrix} \right. \right) = 2k_\rho(x) \quad (9)$$

in (8), we get after a little simplification

$$\int_0^\infty x^{\lambda-1} k_\nu(\alpha x) k_\rho(\beta x^n) G_{p_3, q_3}^{n_3, m_3} \left(\delta x^{2n} \left| \begin{matrix} e_1, \dots, e_{p_3} \\ f_1, \dots, f_{q_3} \end{matrix} \right. \right) dx$$

$$= \frac{2^{\lambda-n-2} (\pi)^{1-n}}{(\alpha)^{\lambda} (n)^{1-\lambda}} S \left[\begin{matrix} \left[\begin{matrix} 2n, 0 \\ 0, 0 \end{matrix} \right] & \left| \begin{matrix} A_1, \dots, A_n, B_1, \dots, B_n; \\ \frac{1}{2}\rho, -\frac{1}{2}\rho \end{matrix} \right. & \frac{\delta (2n)^{2n}}{4(\alpha)^{2n}} \frac{\delta (2n)^{2n}}{(\alpha)^{2n}} \\ \left(\begin{matrix} 0, 2 \\ 0, 0 \end{matrix} \right) & & \\ \left(\begin{matrix} m_3, n_3 \\ p_3-n_3, q_3-n_3 \end{matrix} \right) & \left| \begin{matrix} e_1, \dots, e_{p_3}; f_1, \dots, f_{q_3} \end{matrix} \right. & \end{matrix} \right] \quad (10)$$

where A_k, B_k are defined above, $2(m_3+n_3) > p_3+q_3$

$|\arg \delta| < (m_3+n_3-\frac{1}{2}p_3-\frac{1}{2}q_3)\pi$, $R(\beta) > 0$, $R(\alpha) > 0$,

$R(\lambda \pm \nu \pm n\rho + 2n f_h) > 0$, $h = 1, 2, \dots, n_3$, n is a positive integer.

In case $n = 1$, $\delta = \frac{1}{2}$ and using the formula [2].

$$G_{p,q}^{n,m} \left(x \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) = G_{q,p}^{m,n} \left(x^{-1} \left| \begin{matrix} 1-b_1, \dots, 1-b_q \\ 1-a_1, \dots, 1-a_p \end{matrix} \right. \right) \quad (11)$$

in (10) we get a result due to Sharma [6, p. 364, (3.4)].

Further if we take $m_3 = p_3 = 0$, $n_3 = q_3 = 2$, $f_1 = \frac{1}{2}\mu$, $f_2 = -\frac{1}{2}\mu$ and using (9) in (10), it reduces to the following formula

$$\int_0^\infty x^{\lambda-1} k_\mu(\alpha x) k_\rho(\beta x^n) k_\mu(\delta x^n) dx = \frac{2^{\lambda-n-3} (\pi)^{1-n}}{(\alpha)^\lambda (n)^{1-\lambda}} \\ S \left[\begin{matrix} \left[\begin{matrix} 2n, 0 \\ 0, 0 \end{matrix} \right] \\ \left(\begin{matrix} 0, 2 \\ 0, 0 \end{matrix} \right) \\ \left(\begin{matrix} 0, 2 \\ 0, 0 \end{matrix} \right) \end{matrix} \right] \left[\begin{matrix} A_1, \dots, A_n, B_1, \dots, B_n; \\ ; \frac{1}{2}\rho, -\frac{1}{2}\rho \\ ; \frac{1}{2}\mu, -\frac{1}{2}\mu \end{matrix} \right] \left[\begin{matrix} \frac{\beta^2 (2n)^{2n}}{4(\alpha)^{2n}}, \frac{\delta^2 (2n)^{2n}}{4(\alpha)^{2n}} \end{matrix} \right] \quad (12)$$

where A_k and B_k are defined above. $R(\lambda \pm \mu \pm \rho \pm n \pm \mu n) > 0$, $R(\alpha) > 0$, $R(\beta + \delta) > 0$, n is a positive integer.

In case $n = 1$ and using the formula (9)

$$S \left[\begin{matrix} \left[\begin{matrix} 2, 0 \\ 0, 0 \end{matrix} \right] \\ \left(\begin{matrix} 0, 2 \\ 0, 0 \end{matrix} \right) \\ \left(\begin{matrix} 0, 2 \\ 0, 0 \end{matrix} \right) \end{matrix} \right] \left[\begin{matrix} \nu, \mu; \\ ; \rho, -\rho \\ ; \delta, -\delta \end{matrix} \right] x, y = \sum_{\mu, -\rho} \sum_{\delta, -\delta} \frac{\Gamma(\nu + \rho + \delta) \Gamma(\mu + \rho + \delta)}{\Gamma(-2\rho) \Gamma(-2\delta) x^\rho y^\delta} \\ F_4[\nu + \rho + \delta, \mu + \rho + \delta; 1 + 2\rho, 1 + 2\delta; x, y] \quad (13)$$

in (12), it reduces to a result due to Bailey [1].

From (5), we obtain by using (7)

$$\int_0^\infty x^{\lambda-1} k_\nu(\alpha x) S \left[\begin{matrix} \left[\begin{matrix} 0, 0 \\ 0, 2n \end{matrix} \right] \\ \left(\begin{matrix} m_2, n_2 \\ p_2 - m_2, q_2 - n_2 \end{matrix} \right) \\ \left(\begin{matrix} m_3, n_3 \\ p_3 - m_3, q_3 - n_3 \end{matrix} \right) \end{matrix} \right] \left[\begin{matrix} ; A_1, \dots, A_n, B_1, \dots, B_n \\ c_1, \dots, c_{p_2}; d_1, \dots, d_{q_2} \\ e_1, \dots, e_{p_3}; f_1, \dots, f_{q_3} \end{matrix} \right] \left[\begin{matrix} \beta x^{2n}, \delta x^{2n} \end{matrix} \right] dx$$

$$= \frac{2^{\lambda-n-1} (n)^{\lambda-1}}{(\alpha)^{\lambda} (\pi)^{n-1}} G_{p_2, q_2}^{n_2, m_2} \left(\frac{\beta (2n)^{2n}}{(\alpha)^{2n}} \middle| \begin{matrix} c_1, \dots, c_{p_2} \\ d_1, \dots, d_{q_2} \end{matrix} \right) G_{p_3, q_3}^{n_3, m_3} \left(\frac{\delta (2n)^{2n}}{(\alpha)^{2n}} \middle| \begin{matrix} e_1, \dots, e_{p_3} \\ f_1, \dots, f_{q_3} \end{matrix} \right) \quad (14)$$

$$\text{where } A_k = \Gamma \left(\frac{\lambda + v + 2k}{2n} \right), B_k = \Gamma \left(\frac{\lambda - v + 2k}{2n} \right), k = 0, 1, \dots, (n-1),$$

$2(m_2 + n_2) > p_2 + q_2 + 2n$, $2(m_3 + n_3) > p_3 + q_3 + 2n$, $|\arg \beta| < (m_2 + n_2 - \frac{1}{2} p_2 - \frac{1}{2} q_2 - n) \pi$, $|\arg \delta| < (m_3 + n_3 - \frac{1}{2} p_3 - \frac{1}{2} q_3 - n) \pi$, $m_2 \geq 1$, $m_3 \geq 1$, $R(\lambda \pm v + 2n d_j + 2n f_h) > 0$, $j = 1, 2, \dots, n$, $h = 1, 2, \dots, n_3$, $R(\alpha) > 0$, n is a positive integer.

3. The second formula to be proved is

$$\begin{aligned} & \int_0^\infty x^{\lambda-1} k_v(\alpha x) S \left[\begin{matrix} \left[\begin{matrix} 0, 0 \\ p_1, q_1 \end{matrix} \right] \\ \left(\begin{matrix} m_2, n_2 \\ p_2 - m_2, q_2 - n_2 \end{matrix} \right) \\ \left(\begin{matrix} m_3, n_3 \\ p_3 - m_3, q_3 - n_3 \end{matrix} \right) \end{matrix} \middle| \begin{matrix} a_1, \dots, a_{p_1}; b_1, \dots, b_{q_1} \\ c_1, \dots, c_{p_2}; d_1, \dots, d_{q_2} \\ e_1, \dots, e_{p_3}; f_1, \dots, f_{q_3} \end{matrix} \right] \beta, \delta x^2 \Bigg] dx = \\ & = (\alpha)^{-\lambda} (2)^{\lambda-2} S \left[\begin{matrix} \left[\begin{matrix} 0, 0 \\ p_1, q_1 \end{matrix} \right] \\ \left(\begin{matrix} m_2, n_2 \\ p_2 - m_2, q_2 - n_2 \end{matrix} \right) \\ \left(\begin{matrix} m_3 + 2, n_3 \\ p_3 - m_3, q_3 - n_3 \end{matrix} \right) \end{matrix} \middle| \begin{matrix} a_1, \dots, a_{p_1}; b_1, \dots, b_{q_1} \\ c_1, \dots, c_{p_2}; d_1, \dots, d_{q_2} \\ 1 - \frac{\lambda}{2} \pm \frac{v}{2}, e_1, \dots, e_{p_3}; f_1, \dots, f_{q_3} \end{matrix} \right] \beta, \frac{4\delta}{\alpha^2} \Bigg] \quad (15) \end{aligned}$$

valid for $2(m_2 + n_2) > p_1 + q_1 + p_2 + q_2$, $2(m_3 + n_3) > p_1 + q_1 + p_3 + q_3$, $|\arg \beta| < (m_2 + n_2 - \frac{1}{2} p_1 - \frac{1}{2} p_2 - \frac{1}{2} q_1 - \frac{1}{2} q_2) \pi$, $|\arg \delta| < (m_3 + n_3 - \frac{1}{2} p_1 - \frac{1}{2} q_1 - \frac{1}{2} p_3 - \frac{1}{2} q_3) \pi$, $m_2 \geq 1$, $m_3 \geq 1$, $R(\alpha) > 0$, $R(\lambda \pm v + 2f_h) > 0$, $h = 1, 2, \dots, n_3$.

The proof of (15) is similar to (5).

In case $p_1 = q_1 = 0$ and using the formula (7), (15) reduces to a known result [4, p. 153, eq. 90].

If we take $p_1 = 0$, $q_1 = 1$, $m_2 = 2$, $p_2 = 2$, $n_2 = 1$, $q_2 = 1$, $m_3 = 0$, $n_3 = 1$, $p_3 = 0$, $q_3 = 1$ and using the formulae [9].

$$S \left[\begin{matrix} \left[\begin{matrix} 0, 0 \\ 0, 1 \end{matrix} \right] \\ \left(\begin{matrix} 2, 1 \\ 0, 0 \end{matrix} \right) \\ \left(\begin{matrix} 0, 1 \\ 0, 0 \end{matrix} \right) \end{matrix} \middle| \begin{matrix} ; a \\ 1 - b, 1 - c; 0 \\ ; 0 \end{matrix} \right] x, y = \frac{\Gamma(b) \Gamma(c)}{\Gamma(a)} \Xi_2(b, c; a; -x, -y) \quad (16)$$

and

$$S \left[\begin{array}{c} \left[\begin{array}{cc} 0, 0 \\ 0, 1 \end{array} \right] \\ \left(\begin{array}{cc} 2, 1 \\ 0, 0 \end{array} \right) \\ \left(\begin{array}{cc} 2, 1 \\ 0, 0 \end{array} \right) \end{array} \middle| \begin{array}{c} ; a \\ 1-b, 1-c; 0 \\ 1-d, 1-g; 0 \end{array} \right] x, y = \frac{\Gamma(b) \Gamma(c) \Gamma(d) \Gamma(g)}{\Gamma(a)} \quad (17)$$

$F_3(b, d, c, g; c; -x, -y)$

in (15), we obtain after a little simplification.

$$\int_0^\infty x^{\lambda-1} k_\nu(\alpha x) \Xi_2(\mu, \rho; \rho_1; \beta, \delta x^2) dx = (\alpha)^{-\lambda} 2^{\lambda-2} \Gamma\left(\frac{\lambda}{2} \pm \frac{v}{2}\right) F_3\left(\mu, \frac{\lambda-v}{2}, \rho, \frac{\lambda+v}{2}; \rho_1; \beta, \frac{4\delta}{\alpha^2}\right), \quad (18)$$

valid for $R(\lambda \pm v) > 0$, $R(\alpha) > 2 |R(\sqrt{\delta})|$.

Taking $v = \pm \frac{1}{2}$, (18) reduces to a known result [3, p. 222 eq. (16)].

Now we take $p_1 = 0, q_1 = 1, m_2 = 1, p_2 = 1, n_2 = 1, q_2 = 1, p_3 = 0, m_3 = 0, n_3 = 1, q_3 = 1$ and using the formulae [9].

$$S \left[\begin{array}{c} \left[\begin{array}{cc} 0, 0 \\ 0, 1 \end{array} \right] \\ \left(\begin{array}{cc} 0, 1 \\ 1, 0 \end{array} \right) \\ \left(\begin{array}{cc} 0, 1 \\ 0, 0 \end{array} \right) \end{array} \middle| \begin{array}{c} ; a \\ 1-b; 0 \\ ; 0 \end{array} \right] x, y = \frac{1}{\Gamma(a) \Gamma(1-b)} \phi_3(b; a; x, -y) \quad (19)$$

and

$$S \left[\begin{array}{c} \left[\begin{array}{cc} 0, 0 \\ 0, 1 \end{array} \right] \\ \left(\begin{array}{cc} 1, 1 \\ 1, 0 \end{array} \right) \\ \left(\begin{array}{cc} 0, 1 \\ 1, 0 \end{array} \right) \end{array} \middle| \begin{array}{c} ; a \\ 1-b, 1-c; 0 \\ 1-d; 0 \end{array} \right] x, y = \frac{\Gamma(b)}{\Gamma(a) \Gamma(1-c) \Gamma(1-d)} \Xi_1(b, d, c; a; x, y) \quad (20)$$

in (15) it reduces to the following result.

$$\int_0^\infty x^{\lambda-1} k_\nu(\alpha x) \phi_3(\mu; \rho; \beta, \delta x^2) dx = \Gamma\left(\frac{\lambda}{2} \pm \frac{v}{2}\right) (\alpha)^{-\lambda} 2^{\lambda-2} \Xi_1\left(\frac{\lambda+v}{2}, \mu, \frac{\lambda-v}{2}; \rho; \frac{4\delta}{\alpha^2}, \beta\right), \quad (21)$$

valid for $R(\lambda \pm v) > 0$, $R(a) > 2 \mid R(\sqrt{\delta}) \mid$.

(21) reduces to a known result [3, p. 222, eq. 8] if $v = \pm \frac{1}{2}$.

4. The third formula to be proved is

$$\int_0^\infty x^{\lambda-1} e^{-px} k_v(px) S \left[\begin{matrix} \left[\begin{matrix} 0, 0 \\ p_1, q_1 \end{matrix} \right] \\ \left(\begin{matrix} m_2, n_2 \\ p_2-m_2, q_2-n_2 \end{matrix} \right) \\ \left(\begin{matrix} m_3, n_3 \\ p_3-m_3, q_3-n_3 \end{matrix} \right) \end{matrix} \middle| \begin{matrix} a_1, \dots, a_{p_1}; b_1, \dots, b_{q_1} \\ c_1, \dots, c_{p_2}; d_1, \dots, d_{q_2} \\ e_1, \dots, e_{p_3}; f_1, \dots, f_{q_3} \end{matrix} \right] ax, bx \, dx$$

$$= \frac{(\pi)^{\frac{1}{2}}}{2^\lambda p^\lambda} S \left[\begin{matrix} \left[\begin{matrix} 2, 0 \\ p_1, q_1+1 \end{matrix} \right] \\ \left(\begin{matrix} m_2, n_2 \\ p_2-m_2, q_2-n_2 \end{matrix} \right) \\ \left(\begin{matrix} m_3, n_3 \\ p_3-m_3, q_3-n_3 \end{matrix} \right) \end{matrix} \middle| \begin{matrix} \lambda \pm v, a_1, \dots, a_{p_1}; \lambda + \frac{1}{2}, b_1, \dots, b_{q_1} \\ c_1, \dots, c_{p_2}; d_1, \dots, d_{q_2} \\ e_1, \dots, e_{p_3}; f_1, \dots, f_{q_3} \end{matrix} \right] \frac{a}{2p}, \frac{b}{2p} \quad (22)$$

valid for $2(m_2 + n_2) > p_1 + p_2 + q_1 + q_2$, $2(m_3 + n_3) > p_1 + p_3 + q_1 + q_3$, $|\arg a| < (m_2 + n_2 - \frac{1}{2}p_1 - \frac{1}{2}p_2 - \frac{1}{2}q_1 - \frac{1}{2}q_2) \pi$, $|\arg b| < (m_3 + n_3 - \frac{1}{2}p_1 - \frac{1}{2}p_3 - \frac{1}{2}q_1 - \frac{1}{2}q_3) \pi$, $R(\lambda \pm v + d_j + f_h) > 0$, $j=1, 2, \dots, n_2$, $h=1, 2, \dots, n_3$, $m_2 \geq 1$, $m_3 \geq 1$, $R(p) > 0$. (22) can be proved in the same way as (5) by using (4) instead of (3). Assuming $p_1 = q_1 = 0$ and using the formula (7) in (22), it reduces to the following integral.

$$\int_0^\infty x^{\lambda-1} e^{-px} k_v(px) G_{p_2, q_2}^{n_2, m_2} \left(ax \middle| \begin{matrix} c_1, \dots, c_{p_2} \\ d_1, \dots, d_{q_2} \end{matrix} \right) G_{p_3, q_3}^{n_3, m_3} \left(bx \middle| \begin{matrix} e_1, \dots, e_{p_3} \\ f_1, \dots, f_{q_3} \end{matrix} \right) dx$$

$$= \frac{(\pi)^{\frac{1}{2}}}{2^\lambda p^\lambda} S \left[\begin{matrix} \left[\begin{matrix} 2, 0 \\ 0, 1 \end{matrix} \right] \\ \left(\begin{matrix} m_2, n_2 \\ p_2-m_2, q_2-n_2 \end{matrix} \right) \\ \left(\begin{matrix} m_3, n_3 \\ p_3-m_3, q_3-n_3 \end{matrix} \right) \end{matrix} \middle| \begin{matrix} \lambda - v, \lambda + v; \lambda + \frac{1}{2} \\ c_1, \dots, c_{p_2}; d_1, \dots, d_{q_2} \\ e_1, \dots, e_{p_3}; f_1, \dots, f_{q_3} \end{matrix} \right] \frac{a}{2p}, \frac{b}{2p} \quad (23)$$

valid for $2(m_2 + n_2) > p_2 + q_2$, $2(m_3 + n_3) > p_3 + q_3$, $m_2 \geq 1$, $m_3 \geq 1$, $|\arg a| < (m_2 + n_2 - \frac{1}{2}p_2 - \frac{1}{2}q_2) \pi$, $|\arg b| < (m_3 + n_3 - \frac{1}{2}p_3 - \frac{1}{2}q_3) \pi$, $R(p) > 0$, $R(\lambda \pm v + d_j + f_h) > 0$, $j=1, 2, \dots, n_2$, $h=1, 2, \dots, n_3$.

Taking $v = \pm \frac{1}{2}$, $n_2 = m_2 = 1$, $p_2 = 1$, $q_2 = 1$, $c_1 = \frac{1}{2}$, $d_1 = \rho$, $d_2 = -\rho$ and using the formula [2].

$$\sqrt{\pi} e^{-x} I_v(x) = G_{12}^{11} \left(2x \middle| \begin{matrix} \frac{1}{2} \\ v, -v \end{matrix} \right) \quad (24)$$

in (23), we get after a little adjustment

$$\int_0^\infty x^{\lambda/2-1} e^{-(p^2+\delta^2)x} I_\nu(2p\delta x) G_{q+1, l}^{n, m+1} \left(ax \left| \begin{matrix} 1-\lambda/2, 1-\beta_1, \dots, 1-\beta_q \\ 1-a_1, \dots, 1-a_l \end{matrix} \right. \right) dx$$

$$= \frac{(p-\delta)^{-2\lambda}}{\sqrt{\pi}} S \left[\begin{matrix} \left[\begin{matrix} 1, 0 \\ 0, 0 \end{matrix} \right] \\ \left(\begin{matrix} 1, 1 \\ 0, 1 \end{matrix} \right) \\ \left(\begin{matrix} m+1, n \\ q-m, l-n \end{matrix} \right) \end{matrix} \left| \begin{matrix} \lambda/2 & ; \\ \frac{1}{2} & ; \quad v, -v \\ 1-\lambda/2, 1-\beta_1, \dots, 1-\beta_q; 1-a_1, \dots, 1-a_l \end{matrix} \right. \left. \begin{matrix} \\ \\ \frac{2p\delta}{(p-\delta)^2}, \frac{a}{(p-\delta)^2} \end{matrix} \right] \right] \quad (25)$$

valid for $q + l < 2(m + n + 1)$, $|\arg a| < (m + n + \frac{1}{2} - \frac{1}{2}l - \frac{1}{2}q)\pi$,

$R(p \pm \delta)^2 > 0$, $R(\frac{1}{2}\lambda + v + 1 - a_j) > 0$, $j = 1, 2, \dots, n$.

(25) has been evaluated recently by Maloo [5].

Comparing both the results, we obtain

$$\sum_{r=0}^\infty \frac{b^{r+2r}}{p^{2\lambda+v+2r} \Gamma(1+v+r)r!} G_{l, q+2}^{m+2, n} \left(\frac{p^2}{a} \left| \begin{matrix} a_1, \dots, a_l \\ \lambda+v+r, \lambda+r, \beta_1, \dots, \beta_q \end{matrix} \right. \right)$$

$$= \frac{(p-b)^{-2\lambda}}{\sqrt{\pi}} S \left[\begin{matrix} \left[\begin{matrix} 1, 0 \\ 0, 0 \end{matrix} \right] \\ \left(\begin{matrix} 1, 1 \\ 0, 1 \end{matrix} \right) \\ \left(\begin{matrix} m+1, n \\ q-m, l-n \end{matrix} \right) \end{matrix} \left| \begin{matrix} \lambda & ; \\ \frac{1}{2} & ; \quad v, -v \\ 1-\lambda, 1-\beta_1, \dots, 1-\beta_q; 1-a_1; \dots, 1-a_l \end{matrix} \right. \left. \begin{matrix} \\ \\ \frac{2pb}{(p-b)^2}, \frac{a}{(p-b)^2} \end{matrix} \right] \right] \quad (26)$$

If we use (24) in (23), we get the following result due to Sharma[11].

$$\int_0^\infty x^{\lambda-1} e^{-(p+a+b)x} k_\nu(px) I_\mu(ax) I_\rho(bx) dx$$

$$= \frac{1}{\sqrt{\pi} 2^\lambda p^\lambda} S \left[\begin{matrix} \left[\begin{matrix} 2, 0 \\ 0, 1 \end{matrix} \right] \\ \left(\begin{matrix} 1, 1 \\ 0, 1 \end{matrix} \right) \\ \left(\begin{matrix} 1, 1 \\ 0, 1 \end{matrix} \right) \end{matrix} \left| \begin{matrix} \lambda-v, \lambda+v; \lambda+\frac{1}{2} \\ \frac{1}{2}; \mu, -\mu \\ \frac{1}{2}; \rho, -\rho \end{matrix} \right. \left. \begin{matrix} \\ \\ \frac{a}{p}, \frac{b}{p} \end{matrix} \right] \right] \quad (27)$$

valid for $R(\lambda \pm v + \mu + \rho) > 0$, $R(p) > 0$, $R(p + a + b) > 0$.

Comparing both the results, we obtain a formula for generalised function of two variables.

$$S \left[\begin{array}{c} \left[\begin{array}{c} 2, 0 \\ 0, 1 \end{array} \right] \\ \left(\begin{array}{c} 1, 1 \\ 0, 1 \end{array} \right) \\ \left(\begin{array}{c} 1, 1 \\ 0, 1 \end{array} \right) \end{array} \right]_{\frac{1}{2}} \left| \begin{array}{c} \lambda - v, \lambda + v; \lambda + \frac{1}{2} \\ \mu, -\mu \\ \rho, -\rho \end{array} \right| \frac{a}{p}, \frac{b}{p} \left[\begin{array}{c} \\ \\ \end{array} \right] = \sqrt{\pi}^{-1} \frac{2^{\lambda} \Gamma(-v) \Gamma(\lambda + \mu + \rho + v)}{\Gamma(\mu + 1) \Gamma(\rho + 1)} \frac{p^{\lambda} a^{\mu} b^{\rho}}{2^{1+\mu+\rho+v}} \\ (p+a+b)^{\frac{1}{2}-\lambda-v-\mu-\rho} F_c \left[\frac{\lambda + \mu + \rho + v}{2}, \frac{\lambda + \mu + \rho + v + 1}{2}; v+1, \mu+1, \rho+1; \right. \\ \left. \times \frac{p^2}{(p+a+b)^2}, \frac{a^2}{(p+a+b)^2}, \frac{b^2}{(p+a+b)^2} \right] \quad (28)$$

In (27), if we take $v = \pm \frac{1}{2}$ and compare the result with the formula [3, p. 196], we get

$$S \left[\begin{array}{c} \left[\begin{array}{c} 1, 0 \\ 0, 0 \end{array} \right] \\ \left(\begin{array}{c} 1, 1 \\ 0, 1 \end{array} \right) \\ \left(\begin{array}{c} 1, 1 \\ 0, 1 \end{array} \right) \end{array} \right]_{\frac{1}{2}} \left| \begin{array}{c} \lambda; \\ \mu, -\mu \\ \rho, -\rho \end{array} \right| \frac{2a}{p}, \frac{2b}{p} \left[\begin{array}{c} \\ \\ \end{array} \right] = \frac{\sqrt{\pi}^{-1} 2^{\lambda-1} p^{\lambda} a^{\mu} b^{\rho} \Gamma\left(\frac{\lambda + \mu + \rho}{2}\right) \Gamma\left(\frac{\lambda + \mu + \rho + 1}{2}\right)}{(p+a+b)^{\lambda+\mu+\rho} \Gamma(\mu+1) \Gamma(\rho+1)} \\ F_4 \left(\frac{\lambda + \mu + \rho}{2}, \frac{\lambda + \mu + \rho + 1}{2}; \mu+1, \rho+1; \frac{a^2}{(p+a+b)^2}, \frac{b^2}{(p+a+b)^2} \right) \quad (29)$$

Taking $p_1 = 0, q_1 = 1, a_1 = \lambda - v, m_2 = 0, p_2 = 1, n_2 = 1, q_2 = 1, m_3 = 0, p_3 = 1, n_3 = 1, q_3 = 1$ and using the formulae [9].

$$S \left[\begin{array}{c} \left[\begin{array}{c} 1, 0 \\ 0, 1 \end{array} \right] \\ \left(\begin{array}{c} 0, 1 \\ 1, 0 \end{array} \right) \\ \left(\begin{array}{c} 0, 1 \\ 1, 0 \end{array} \right) \end{array} \right] \left| \begin{array}{c} \lambda; \mu \\ 1 - \rho; 0 \\ 1 - \delta; 0 \end{array} \right| x, y \left[\begin{array}{c} \\ \\ \end{array} \right] = \frac{\Gamma(\lambda)}{\Gamma(\mu) \Gamma(1 - \rho) \Gamma(1 - \delta)} \\ F_1(\lambda, \rho, \delta; \mu; x, y) \quad (30)$$

and

$$S \left[\begin{array}{c} \left[\begin{array}{c} 0, 0 \\ 0, 1 \end{array} \right] \\ \left(\begin{array}{c} 0, 1 \\ 1, 0 \end{array} \right) \\ \left(\begin{array}{c} 0, 1 \\ 1, 0 \end{array} \right) \end{array} \right] \left| \begin{array}{c} ; \lambda \\ 1 - \rho; 0 \\ 1 - \delta; 0 \end{array} \right| x, y \left[\begin{array}{c} \\ \\ \end{array} \right] = \frac{1}{\Gamma(1 - \rho) \Gamma(1 - \delta) \Gamma(\lambda)} \\ \phi_2(\rho, \delta; c; x, y) \quad (31)$$

in (22), we obtain

$$\int_0^\infty x^{\lambda-1} e^{-\frac{1}{2}\mu x} k_\nu\left(\frac{1}{2}px\right) \phi_2(\rho, \delta; \lambda - \nu; ax, bx) dx$$

$$= \frac{\sqrt{\pi} \Gamma(\lambda \pm \frac{1}{2})}{p^\lambda \Gamma(\lambda + \frac{1}{2})} F_1\left(\lambda + \nu, \rho, \delta; \lambda + \frac{1}{2}; \frac{a}{p}, \frac{b}{p}\right), \quad (32)$$

valid for $R(\lambda \pm \nu) > 0$, $R(p) > 0$, $R(p) > R(a)$, $R(b)$.

Taking $\nu = \pm \frac{1}{2}$, (32) reduces to a known result [3, p. 222, Eq. (4)].

Assuming $p_1 = 0$, $q_1 = 1$, $b_1 = \lambda + \nu$, $m_2 = n_2 = p_2 = q_2 = 1$, $m_3 = p_3 = 0$, $n_3 = q_3 = 1$ and using the formulae (19) and [9]

$$S \left[\begin{array}{c} \left[\begin{array}{c} 1, 0 \\ 0, 1 \end{array} \right] \\ \left(\begin{array}{c} 1, 1 \\ 0, 0 \end{array} \right) \\ \left(\begin{array}{c} 0, 1 \\ 0, 0 \end{array} \right) \end{array} \middle| \begin{array}{c} \lambda; \mu \\ 1 - \rho; 0 \\ ; 0 \end{array} \right] x, y = \frac{\Gamma(\lambda) \Gamma(\rho)}{\Gamma(\mu)} \phi_1(\lambda, \rho; \mu; -x, -y) \quad (33)$$

in (22) we obtain

$$\int_0^\infty x^{\lambda-1} e^{-\frac{1}{2}\mu x} k_\nu\left(\frac{1}{2}px\right) \phi_3(\mu; \lambda + \nu; ax, bx) dx$$

$$= \frac{\sqrt{\pi} \Gamma(\lambda \pm \frac{1}{2})}{p^\lambda \Gamma(\lambda + \frac{1}{2})} \phi_1(\lambda - \nu, \mu; \lambda + \frac{1}{2}; \frac{a}{p}, \frac{b}{p}), \quad (34)$$

valid for $R(\lambda \pm \nu) > 0$, $R(p) > 0$, $R(a)$, $R(b)$.

Taking $\nu = \pm \frac{1}{2}$, it reduces to a known result [3, p. 222, Eq. 9].

In last we take $p_1 = 1$, $q_1 = 0$, $m_2 = m_3 = p_2 = p_3 = 0$, $n_2 = n_3 = 1$, $q_2 = q_3 = 2$, $a_1 = \lambda + \frac{1}{2}$, $d_1 = 0$, $d_2 = 1 - \mu$, $f_1 = 0$, $f_2 = 1 - \rho$ and using the formulae [9]

$$S \left[\begin{array}{c} \left[\begin{array}{c} 1, 0 \\ 1, 0 \end{array} \right] \\ \left(\begin{array}{c} 0, 1 \\ 0, 1 \end{array} \right) \\ \left(\begin{array}{c} 0, 1 \\ 0, 1 \end{array} \right) \end{array} \middle| \begin{array}{c} \lambda, \mu; \\ ; 0, 1 - \rho \\ ; 0, 1 - \delta \end{array} \right] x, y = \frac{\Gamma(\lambda)}{\Gamma(1 - \mu) \Gamma(\rho) \Gamma(\delta)}$$

$$F_4(\lambda, \mu; \rho, \delta; x, y) \quad (35)$$

and

$$S \left[\begin{array}{c} \left[\begin{array}{c} 1, 0 \\ 0, 0 \end{array} \right] \\ \left(\begin{array}{c} 0, 1 \\ 0, 1 \end{array} \right) \\ \left(\begin{array}{c} 0, 1 \\ 0, 1 \end{array} \right) \end{array} \middle| \begin{array}{c} \lambda; \\ , 0, 1 - \rho \\ ; 0, 1 - \delta \end{array} \right] x, y = \frac{\Gamma(\lambda)}{\Gamma(\rho) \Gamma(\delta)}$$

$$\psi_2(\lambda; \rho, \delta; x, y) \quad (36)$$

in (22), we get

$$\int_0^{\infty} x^{\lambda-1} e^{-px} k_v(px) \psi_2\left(\lambda + \frac{1}{2}; \rho, \mu; ax, bx\right) dx$$

$$= \frac{\sqrt{\pi} \Gamma(\lambda \pm v)}{(2p)^\lambda \Gamma(\lambda + \frac{1}{2})} F_4\left(\lambda + v, \lambda - v; \rho, \mu; \frac{a}{2p}, \frac{b}{2p}\right) \quad (37)$$

valid for $R(\lambda \pm v) > 0$, $R(2p) > 0$, $R(a)$, $R(b)$. Assuming $v = \pm \frac{1}{2}$, we obtain a known result [3, p. 222, eq. (13)].

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On the Solution of Simultaneous Dual Series Equations

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Abstract

The solution of the simultaneous dual series equations

$$\sum_{n=1}^{\infty} \sum_{j=1}^s a_{ij}(\alpha_n) b_{nj} J_{\mu_i}(\alpha_n r) = f_i(r), \quad 0 < r < 1,$$

$$\sum_{n=1}^{\infty} \sum_{j=1}^s c_{ij}(\alpha_n) b_{nj} J_{\mu_i}(\alpha_n r) = g_i(r), \quad 1 < r < d;$$

$$i = 1, 2, \dots, s,$$

where $\{\alpha_n\}$ is the sequence of positive zeros of the Bessel function $J_{\mu_i}(d\alpha)$, arranged in order of increasing magnitude, μ_i are real numbers, $a_{ij}(\alpha_n)$, $c_{ij}(\alpha_n)$, $f_i(r)$, $g_i(r)$ are known functions of the variables indicated, is obtained by taking a representation of the unknown constants b_{nj} in the form of Neumann series of Bessel functions whose coefficients are determined by means of an infinite series of linear equations.

1. Introduction

In the analysis of certain problems in mathematical physics in which Fourier-Bessel expansions are involved we are sometimes led to the solution of the dual series equations of the form

$$\sum_{n=1}^{\infty} \alpha_n^{-p} b_n J_{\mu}(\alpha_n r) = f(r), \quad 0 < r < 1, \quad (1.1)$$

$$\sum_{n=1}^{\infty} b_n J_{\mu}(\alpha_n r) = g(r), \quad 1 < r < d, \quad (1.2)$$

where $\{\alpha_n\}$ are the positive zeros of the Bessel function $J_{\mu}(d\alpha)$ arranged in order of increasing magnitude, p and μ are real constants, the functions $f(r)$ and $g(r)$ are known, and the sequence of real constants $\{b_n\}$ is to be determined.

The particular case of the equations (1.1) and (1.2) in which $g(r) \equiv 0$ has been considered by Cook and Tranter (1959) by assuming a representation of b_n in the form of Neumann series of Bessel functions and determining the coefficients by means of an infinite series of linear equations. Recently Sneddon and Srivastava (1964) assumed an integral representation of b_n in terms of a single function $\psi(t)$ and then reduced the problem to that of solving a Fredholm integral equation of the second kind for the auxiliary function $\psi(t)$.

In this paper we obtain the solution of the simultaneous dual series equations

$$\sum_{n=1}^{\infty} \sum_{j=1}^s a_{ij}(\alpha_n) b_{nj} J_{\mu_i}(\alpha_n r) = f_i(r), \quad 0 < r < 1, \quad (1.3)$$

$$\sum_{n=1}^{\infty} \sum_{j=1}^s c_{ij}(\alpha_n) b_{nj} J_{\mu_i}(\alpha_n r) = g_i(r), \quad 1 < r < d; \quad (1.4)$$

$$i = 1, 2, \dots, s,$$

where $\{\alpha_n\}$ are the positive zeros of the Bessel function $J_{\mu_i}(d\alpha)$, arranged in order of increasing magnitude, μ_i are real numbers; $a_j(\alpha_n)$, $c_{ij}(\alpha_n)$, $f_i(r)$ and $g_i(r)$ are known functions, by assuming a representation of b_{nj} in the form of Neumann series of Bessel functions and following the method used by Erdogan and Bahar (1964) in the case of dual integral equations.

As in most of the work of this type, the analysis is formal. No attempt has been made to justify the change of order of summation and hence the conditions on the parameters involved in such processes are not reflected in restrictions on the parameters.

2. Consider the dual series equations

$$\sum_{n=1}^{\infty} \sum_{j=1}^s a_{ij}(\alpha_n) b_{nj} J_{\mu_i}(\alpha_n r) = f_i(r), \quad 0 < r < 1, \quad (2.1)$$

$$\sum_{n=1}^{\infty} \sum_{j=1}^s c_{ij}(\alpha_n) b_{nj} J_{\mu_i}(\alpha_n r) = g_i(r), \quad 1 < r < d; \quad (2.2)$$

$$i = 1, 2, \dots, s.$$

These equations, on using the result [Watson (1958), p. 576, eq. (4)] reduce to

$$\sum_{n=1}^{\infty} \sum_{j=1}^s A_{ij}(\alpha_n) B_{nj} J_{\mu_i}(\alpha_n r) = F_i(r), \quad 0 < r < 1, \quad (2.3)$$

$$\sum_{n=1}^{\infty} B_{ni} J_{\mu_i}(\alpha_n r) = 0, \quad 1 < r < d; \quad i = 1, 2, \dots, s, \quad (2.4)$$

where

$$B_{ni} = \sum_{j=1}^s c_{ij}(\alpha_n) b_{nj} - \frac{2}{d^2 J_{\mu_i+1}^2(\alpha_n d)} \int_1^d t g_i(t) J_{\mu_i}(\alpha_n t) dt, \quad (2.4')$$

$$A_{ij}(\alpha_n) = a_{ij}(\alpha_n) / c_{ij}(\alpha_n),$$

$$F_i(r) = f_i(r) - \frac{2}{d^2} \sum_{n=1}^{\infty} \sum_{j=1}^s A_{ij}(\alpha_n) J_{\mu_i}(\alpha_n r) \frac{1}{J_{\mu_j+1}^2(\alpha_n d)} \int_1^d t g_j(t) J_{\mu_j}(\alpha_n t) dt.$$

By virtue of the relation [Tranter (1959)]

$$\sum_{n=1}^{\infty} \frac{J_{\mu_j+2m+1+\frac{1}{2}}(\alpha_n) J_{\mu_j}(\alpha_n r)}{\alpha_n^{1+\frac{1}{2}} J_{\mu_j+1}^2(\alpha_n d)} = 0, \quad 1 < r < d, \quad (2.5)$$

it is evident that

$$B_{nj} = \frac{1}{\alpha_n^{1+\frac{1}{2}p_j} J^2 \mu_{j+1}(\alpha_n d)} \sum_{m=0}^{\infty} D_{mj} J^{\mu_j+2m+1+\frac{1}{2}p_j}(\alpha_n), \quad (2.6)$$

$$j = 1, 2, \dots, s;$$

provided $Re(\mu_j) > -1$, $(1 + \frac{1}{2}p_j)$ real and positive; is a solution of the equation (2.4).

On substituting this value of B_{nj} in (2.3), we have

$$\sum_{m=0}^{\infty} \sum_{j=1}^s D_{mj} \sum_{n=1}^{\infty} A_{ij}(\alpha_n) \frac{J^{\mu_j+2m+1+\frac{1}{2}p_j}(\alpha_n) J^{\mu_i}(\alpha_n r)}{\alpha_n^{1+\frac{1}{2}p_j} J^2 \mu_{j+1}(\alpha_n d)} = F_i(r), \quad 0 < r < 1,$$

$$i = 1, 2, \dots, s, \quad (2.7)$$

assuming that the necessary convergence requirements are fulfilled.

Multiplying both sides of (2.7) by

$r^{\mu_i+1} (1-r^2)^{\frac{1}{2}p_i} F_k(1 + \frac{1}{2}p_i + \mu_i, \mu_i + 1; r^2)$, $k = 0, 1, 2, \dots$,
and integrating in r from 0 to 1 and on using the result [Tranter (1962), p. 313]

$$\int_0^1 r^{\mu_i+1} (1-r^2)^{1/2p_i} F_k(1 + \frac{1}{2}p_i + \mu_i, \mu_i + 1; r^2) J^{\mu_i}(\alpha_n r) dr$$

$$= \alpha_n^{-1-1/2p_i} J^{\mu_i+2k+1+1/2p_i}(\alpha_n) \frac{2^{1/2p_i} \Gamma(\mu_i + 1) \Gamma(1 + k + \frac{1}{2}p_i)}{\Gamma(1 + k + \mu_i)}$$

we obtain

$$\sum_{m=0}^{\infty} \sum_{j=1}^s D_{mj} \sum_{n=1}^{\infty} A_{ij}(\alpha_n) \frac{J^{\mu_i+2k+1+\frac{1}{2}p_i}(\alpha_n) J^{\mu_j+2m+1+\frac{1}{2}p_j}(\alpha_n)}{\alpha_n^{2+1/2p_i+1/2p_j} J^2 \mu_{j+1}(\alpha_n d)}$$

$$= E(\mu_i, p_i, k) \quad i = 1, 2, \dots, s; k = 0, 1, 2, \dots, \quad (2.8)$$

where

$$E(\mu_i, p_i, k) = \frac{\Gamma(\mu_i + k + 1)}{2^{\frac{1}{2}p_i} \Gamma(\mu_i + 1) \Gamma(1 + k + \frac{1}{2}p_i)} \int_0^1 r^{\mu_i+1} (1-r^2)^{\frac{1}{2}p_i}$$

$$\times F_k(1 + \frac{1}{2}p_i + \mu_i, \mu_i + 1; r^2) F_i(r) dr, \quad (2.9)$$

and F_k is the Jacobi polynomial which is defined in terms of hypergeometric series by the relation [Magnus and Oberhettinger (1954), p. 83]

$$F_k(\alpha, \gamma; x) = {}_2F_1(-k, \alpha + k; \gamma; x).$$

The equation (2.8) provides a set of algebraic equations to determine the coefficients D_{mj} . Once the values of D_{mj} have been found from this set, the coefficients B_{nj} can be evaluated from equation (2.6).

For computational purposes we can write (2.8) in a more convenient form by adding to and subtracting from the left hand side the sum of series [Sneddon and Srivastav (1964), § 3]

$$2/d^2 \sum_{m=0}^{\infty} D_{mi} \sum_{n=1}^{\infty} \frac{J^{\mu_i+2k+1+\frac{1}{2}p_i}(\alpha_n) J^{\mu_i+2m+1+\frac{1}{2}p_i}(\alpha_n)}{\alpha_n^2 J^2 \mu_{i+1}(\alpha_n d)}$$

$$\begin{aligned}
&= D_{ik} \left(\frac{1}{(2\mu_i + 4k + 2 + p_i)} + 2/\pi \sin \frac{1}{2} p_i \pi \int_0^\infty \frac{K_{\mu_i}(dt)}{t I_{\mu_i}(dt)} I^2_{\mu_i + 2k + 1 + \frac{1}{2} p_i}(t) dt \right), \\
&2/d^2 \sum_{m=0}^\infty \sum_{\substack{j=1 \\ j \neq i}}^s D_{mj} \sum_{n=1}^\infty \frac{I_{\mu_i + 2k + 1 + \frac{1}{2} p_i}(\alpha_n) J_{\mu_j + 2m + 1 + \frac{1}{2} p_j}(\alpha_n)}{\alpha_n^2 J^2_{\mu_j + 1}(\alpha_n d)} \\
&= \sum_{m=0}^\infty \sum_{\substack{j=1 \\ j \neq i}}^s D_{mj} \left(\frac{2}{\pi} \cdot \frac{\sin(\mu_i - \mu_j + 2k - 2m + \frac{1}{2} p_i - \frac{1}{2} p_j) \pi/2}{(\mu_i + 2k + 1 + \frac{1}{2} p_i)^2 - (\mu_j + 2m + 1 + \frac{1}{2} p_j)^2} \right. \\
&\quad \left. + 2/\pi \sin \left\{ (\mu_i - \mu_j + 2k + 2m + \frac{1}{2} p_i + \frac{1}{2} p_j) \pi/2 \right\} \int_0^\infty \frac{K_{\mu_i}(dt)}{t I_{\mu_j}(dt)} \right. \\
&\quad \left. \times I_{\mu_i + 2k + 1 + \frac{1}{2} p_i}(t) I_{\mu_j + 2m + 1 + \frac{1}{2} p_j}(t) dt \right).
\end{aligned}$$

Thus we obtain

$$\begin{aligned}
&D_{ik} \left(\frac{1}{(2\mu_i + 4k + 2 + p_i)} + 2/\pi \sin \frac{1}{2} p_i \pi \int_0^\infty \frac{K_{\mu_i}(dt)}{t I_{\mu_i}(dt)} I^2_{\mu_i + 2k + 1 + \frac{1}{2} p_i}(t) dt \right) \\
&+ \sum_{m=0}^\infty \sum_{\substack{j=1 \\ j \neq i}}^s D_{mj} \left(\frac{2}{\pi} \cdot \frac{\sin(\mu_i - \mu_j + 2k - 2m + \frac{1}{2} p_i - \frac{1}{2} p_j) \pi/2}{(\mu_i + 2k + 1 + \frac{1}{2} p_i)^2 - (\mu_j + 2k + 1 + \frac{1}{2} p_j)^2} \right. \\
&\quad \left. + \frac{2}{\pi} \sin(\mu_i - \mu_j + 2k + 2m + \frac{1}{2} p_i + \frac{1}{2} p_j) \pi/2 \int_0^\infty \frac{K_{\mu_j}(dt)}{t I_{\mu_j}(dt)} \right. \\
&\quad \left. \times I_{\mu_i + 2k + 1 + \frac{1}{2} p_i}(t) I_{\mu_j + 2m + 1 + \frac{1}{2} p_j}(t) dt \right) \\
&+ \sum_{m=0}^\infty D_{mi} \left[\sum_{n=1}^\infty \left(\frac{A_{ij}(\alpha_n)}{\alpha_n^{2\mu_i}} - \frac{2}{d^2} \right) \frac{J_{\mu_i + 2k + 1 + \frac{1}{2} p_i}(\alpha_n) J_{\mu_i + 2m + 1 + \frac{1}{2} p_i}(\alpha_n)}{\alpha_n^2 J^2_{\mu_i + 1}(\alpha_n d)} \right] \\
&+ \sum_{m=0}^\infty \sum_{\substack{j=1 \\ j \neq i}}^s D_{mj} \left[\sum_{n=1}^\infty \left(\frac{A_{ij}(\alpha_n)}{\alpha_n^{\frac{1}{2} p_i + \frac{1}{2} p_j}} - \frac{2}{d^2} \right) \frac{J_{\mu_i + 2k + 1 + \frac{1}{2} p_i}(\alpha_n) J_{\mu_j + 2m + 1 + \frac{1}{2} p_j}(\alpha_n)}{\alpha_n^2 J^2_{\mu_j + 1}(\alpha_n d)} \right] \\
&= E(\mu_i, p_i, k) \quad i = 1, 2, \dots, s; \quad k = 0, 1, 2, \dots \quad (2.10)
\end{aligned}$$

In particular, if we take $\mu_i = \frac{1}{2}$ and write $d = \pi/e$, $r = x/e$, $b_{nj} = \sqrt{n} b'_{nj}$, $f_i(r) = \sqrt{\{2/(\pi x)\}} F_i(x)$ and $g_i(r) = \sqrt{\{2/(\pi x)\}} G_i(x)$; solution of the simultaneous dual series equations with sine kernels

$$\sum_{n=1}^\infty \sum_{j=1}^s a_{ij}(ne) b'_{nj} \sin nx = F_i(x), \quad 0 < x < e, \quad (2.11)$$

$$\sum_{n=1}^\infty \sum_{j=1}^s c_{ij}(ne) b'_{nj} \sin nx = G_i(x), \quad e < x < \pi, \quad (2.12)$$

$$i = 1, 2, \dots, s,$$

is given by

$$B'_{nj} = \frac{1}{(ne)^{3/2} J_{3/2}^2(n\pi)} \sum_{m=0}^{\infty} D_{mj} J_{2m+2}(ne), \quad (2.13)$$

$$j = 1, 2, \dots, s;$$

where

$$B'_{ni} = \sum_{j=1}^s c_{ij}(ne) b'_{nj} - \frac{2}{\pi} \int_e^{\pi} G_i(t) \sin nt \, dt,$$

and the coefficients D_{mj} are determined from the equation

$$\sum_{m=0}^{\infty} \sum_{j=1}^s D_{mj} \sum_{n=1}^{\infty} \frac{a_{ij}(ne)}{c_{ij}(ne)} \frac{J_{2k+2}(ne)}{(ne)^3 J_{3/2}^2(n\pi)} \frac{J_{2m+2}(ne)}{(ne)^3 J_{3/2}^2(n\pi)}$$

$$= \sqrt{2/\pi} \int_0^e \sqrt{x/e} \sin \{(2m+2) \arcsin x/e\} H_i(x) \, dx/e \quad (2.14)$$

where

$$H_i(x) = I_i(x) - 2/\pi \sum_{n=1}^{\infty} \sum_{j=1}^s a_{ij}(ne)/c_{ij}(ne) \sin nx \int_e^{\pi} G_j(t) \sin nt \, dt.$$

Similarly if we take $\mu_i = -\frac{1}{2}$, the solution of the dual series equations with cosinc kernels

$$\sum_{n=1}^{\infty} \sum_{j=1}^s a_{ij}(ne) b'_{nj} \cos(n - \frac{1}{2})x = I_i(x), \quad 0 < x < e, \quad (2.15)$$

$$\sum_{n=1}^{\infty} \sum_{j=1}^s c_{ij}(ne) b'_{nj} \cos(n - \frac{1}{2})x = G_i(x), \quad e < x < \pi, \quad (2.16)$$

$$i = 1, 2, \dots, s;$$

is given by

$$B'_{nj} = \frac{1}{(ne)^{3/2} J_{1/2}^2(n\pi)} \sum_{m=0}^{\infty} D_{mj} J_{2m+1}(ne), \quad (2.17)$$

$$j = 1, 2, \dots, s;$$

where

$$B'_{ni} = \sum_{j=1}^s c_{ij}(ne) b'_{nj} - \frac{2}{\pi} \int_e^{\pi} G_i(t) \cos(n - \frac{1}{2})t \, dt,$$

and the coefficients D_{mj} are determined from the equation

$$\sum_{m=0}^{\infty} \sum_{j=1}^s D_{mj} \sum_{n=1}^{\infty} \frac{a_{ij}(ne)}{c_{ij}(ne)} \frac{J_{2k+1}(ne)}{(ne)^3 J_{1/2}^2(n\pi)} \frac{J_{2m+1}(ne)}{(ne)^3 J_{1/2}^2(n\pi)}$$

$$= \sqrt{2/\pi} \int_0^e \sqrt{x/e} \, 1/e \cos \{(2k+1) \arcsin x/e\} H_i(x) \, dx \quad (2.18)$$

where

$$H_i(x) = F_i(x) - 2/\pi \sum_{n=1}^{\infty} \sum_{j=1}^s a_{ij}(ne)/c_{ij}(ne) \cos(n - \frac{1}{2})x \\ \times \int_0^{\pi} G_j(t) \cos(n - \frac{1}{2})t dt.$$

The solution of the simultaneous dual series equations with trigonometric kernels can also be obtained independently.

As an example, if we take

$$A_{ij}(\alpha_n) = \sum_q C_{ijq} \alpha_n^{\lambda_{ijq}},$$

and if $\lambda_{ij} \geq \lambda_{ijq}$, then by taking

$$-(\mu_i + 2k + \frac{1}{2}p_j + \mu_j + 2m + \frac{1}{2}p_j + 3) < \lambda_{ij} - \frac{1}{2}p_i - \frac{1}{2}p_j - 2 \leq 0$$

all the series within the square brackets in (2.10) are convergent and are readily evaluated by using the result [Sneddon and Srivastava (1964), eq. (3.3)]

$$\frac{2}{d^2} \sum_{n=1}^{\infty} \frac{J_{\alpha}(\lambda_n) J_{\beta}(\lambda_n)}{J_{2\nu+1}^2(\lambda_n d)} \lambda_n^{\gamma} = \int_0^{\infty} J_{\alpha}(x) J_{\beta}(x) x^{1+\gamma} dx \\ + \frac{2}{\pi} \sin\{(\alpha + \beta + \gamma - 2\nu)\pi/2\} \cdot \int_0^{\infty} \frac{K_{\nu}(dy)}{I_{\nu}(dy)} J_{\alpha}(y) I_{\beta}(y) y^{1+\gamma} dy,$$

provided $d > 1$, $-(\alpha + \beta + 1) < \gamma \leq 0$.

3. In this section we reduce the equations (1.3) and (1.4) into a singular integral equation which can be solved by well tried procedures.

Let us assume that

$$\sum_{n=1}^{\infty} B_{ni} J_{\mu_i}(\alpha_n r) = \begin{cases} P_i(r), & 0 < r < 1, \\ 0, & 1 < r < d, \end{cases} \quad i = 1, 2, \dots, s; \quad (3.1)$$

then, on using the formula for the coefficients in a Fourier-Bessel expansion [Watson (1958), p. 576] the coefficients B_{ni} are given by

$$B_{ni} = \frac{2}{d^2 J_{\mu_i+1}^2(\alpha_n d)} \int_0^1 t P_i(t) J_{\mu_i}(\alpha_n t) dt. \quad (3.2)$$

On substituting (3.2) into (2.3) and assuming that the change of order of summation is permitted, we obtain

$$\sum_{j=1}^s \int_0^1 M_{ij}(r, t) P_j(t) t dt = H_i(r), \quad 0 < r < 1; \quad (3.3)$$

$$i = 1, 2, \dots, s,$$

where

$$M_{ij}(r, t) = 2 \sum_{n=1}^{\infty} c_{ij}(\alpha_n) \frac{J_{\mu_i}(\alpha_n r) J_{\mu_i}(\alpha_n t)}{d^2 J_{\mu_j+1}^2(\alpha_n d)}.$$

The equation (3.3) is a singular integral equation in $P_i(t)$ which can be solved by well known methods. Knowing the value of $P_i(t)$, the value of B_{ni} can be obtained from (3.2) and hence the solution of the equations (1.3) and (1.4) can be determined from the equation (2.4').

Acknowledgement

The author wishes to record his deep sense of gratitude to Prof. Ram Kumar for his kind guidance and constant help in the preparation of this paper.

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Precipitation of Hydrus Cadmium Oxide II. $\text{CdSO}_4 - \text{NH}_4 \text{OH}$ System

By

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[Received on 13th December, 1966]

Abstract

The precipitation of hydrus cadmium oxide by ammonium hydroxide has been studied. It is observed that with the progressive addition of ammonium hydroxide to a solution of cadmium sulphate, various hydroxy sulphates are successively precipitated, finally resulting into cadmium hydroxide. Here there is also an evidence for the precipitation of a compound of probable formula $\text{Cd}(\text{OH})(\text{SO}_4)_{0.5} \times \text{H}_2\text{O}, y\text{NH}_3$, in which $\text{Cd}^{++}; \text{OH}^-$ ratio is equal to 1 : 1. At the same time the formation of the complex amine also plays its part, so that an appreciable quantity of cadmium is left in solution.

Introduction

In earlier publication¹ from this laboratory, results were reported on the precipitation of hydrus cadmium oxide by sodium hydroxide from a solution of cadmium sulphate. The present paper deals with a similar study of the precipitation of hydrus cadmium oxide by ammonium hydroxide. It is observed, that, in general, the behaviour is similar to sodium hydroxide, except that the results are influenced by the formation of cadmium amine complexes.

Experimental

Precipitation Studies

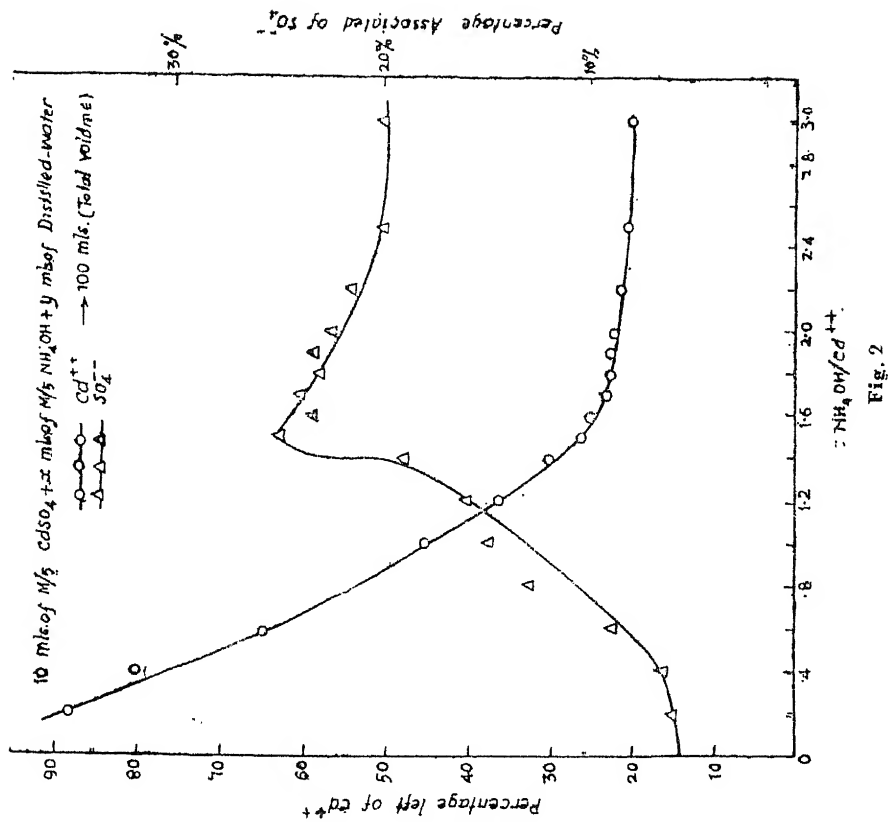
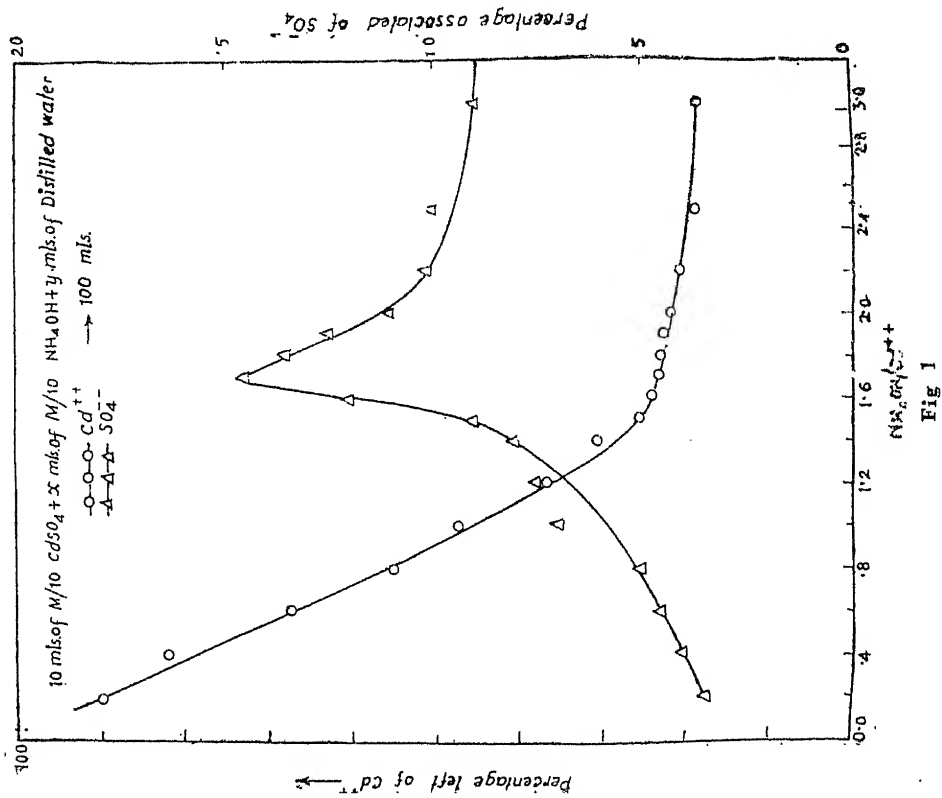
(a) *Analytical Study.*—Varying amounts of standard ammonium hydroxide solution were added to a fixed volume (10 mls) of standard (0.1 M, 0.2 M) cadmium sulphate solution in 100 mls. volumetric flasks, and next day in the centrifugate cadmium and sulphate were estimated as given in the earlier publication¹. The results are graphically represented in Figs. 1 and 2.

(b) *Examination of Precipitate.*—Further to understand fully the real nature of associated sulphate in hydrus cadmium oxide precipitate, the precipitates obtained have been analyzed for their Cd^{++} and SO_4^{--} contents as done earlier.¹ From the results obtained the amounts of precipitated Cd^{++} , associated SO_4^{--} in both washed and unwashed samples were calculated. The results are graphically represented in Fig. No. 3, but here unprecipitated Cd^{++} has been plotted in place of precipitated Cd^{++} . Unprecipitated Cd^{++} has been calculated by subtracting the amount of precipitated Cd^{++} in the washed precipitate from the total cadmium taken in the experiment.

(c) *Physico-chemical Study.*—Mixtures of cadmium sulphate and ammonium hydroxide of different concentrations were prepared as outlined above, and after one day their pH and conductance were measured. Conductance measurements have been done throughout at $30.0 \pm 0.1^\circ\text{C}$ by Leeds and Northrup Conductance Bridge using audiofrequency oscillator. pH measurements were done by a Leeds and Northrup pH meter. The results are graphically represented in Figs. 4 and 5.

Studies of Ageing.

To study the effect of ageing on these precipitates a set of above reaction mixtures (containing 5 mls. of 0.1 M CdSO_4) was allowed to age, and the pH and conductance of the solutions were measured at different intervals of time (15 mts., 2 hrs., one day and nine days) after precipitation. The results are plotted in Figs. 6 and 7.



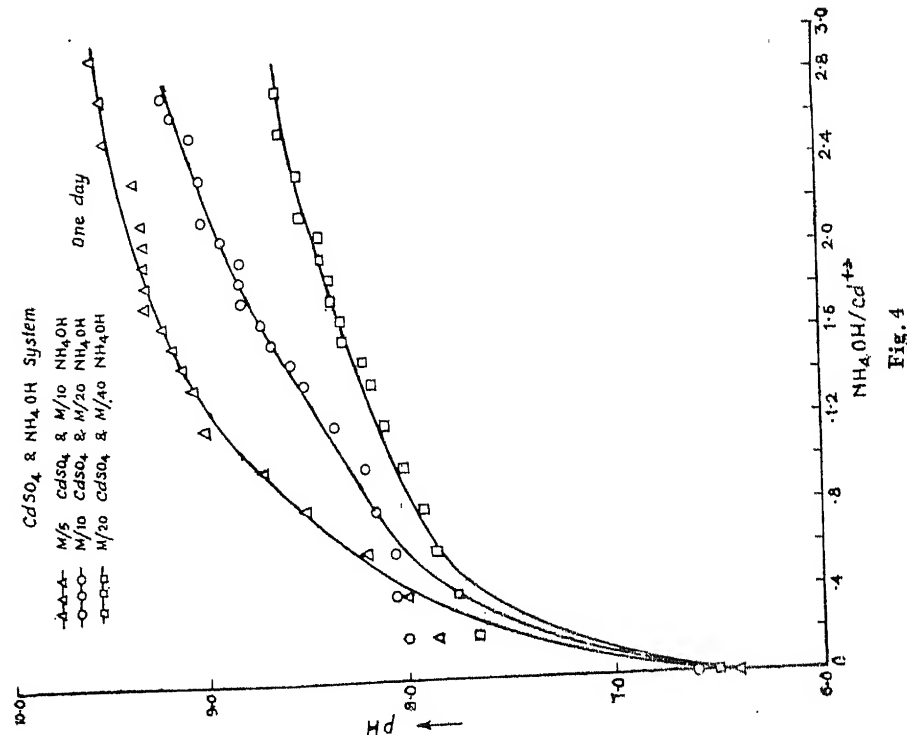


Fig. 4

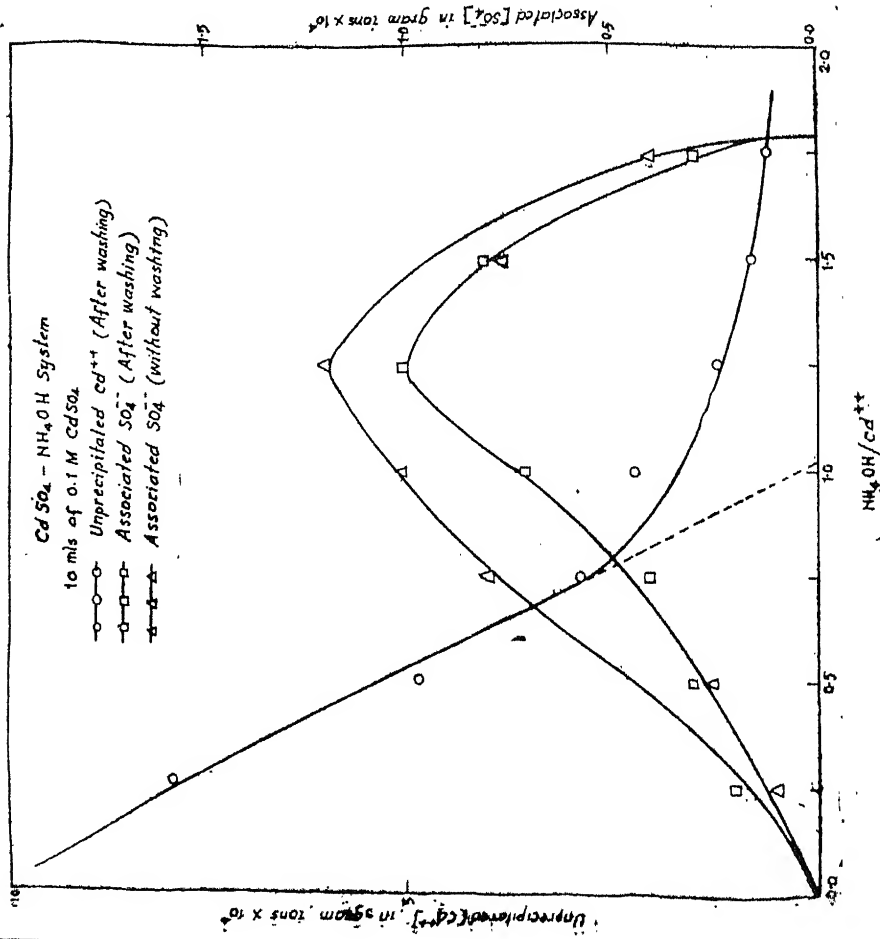


Fig. 3

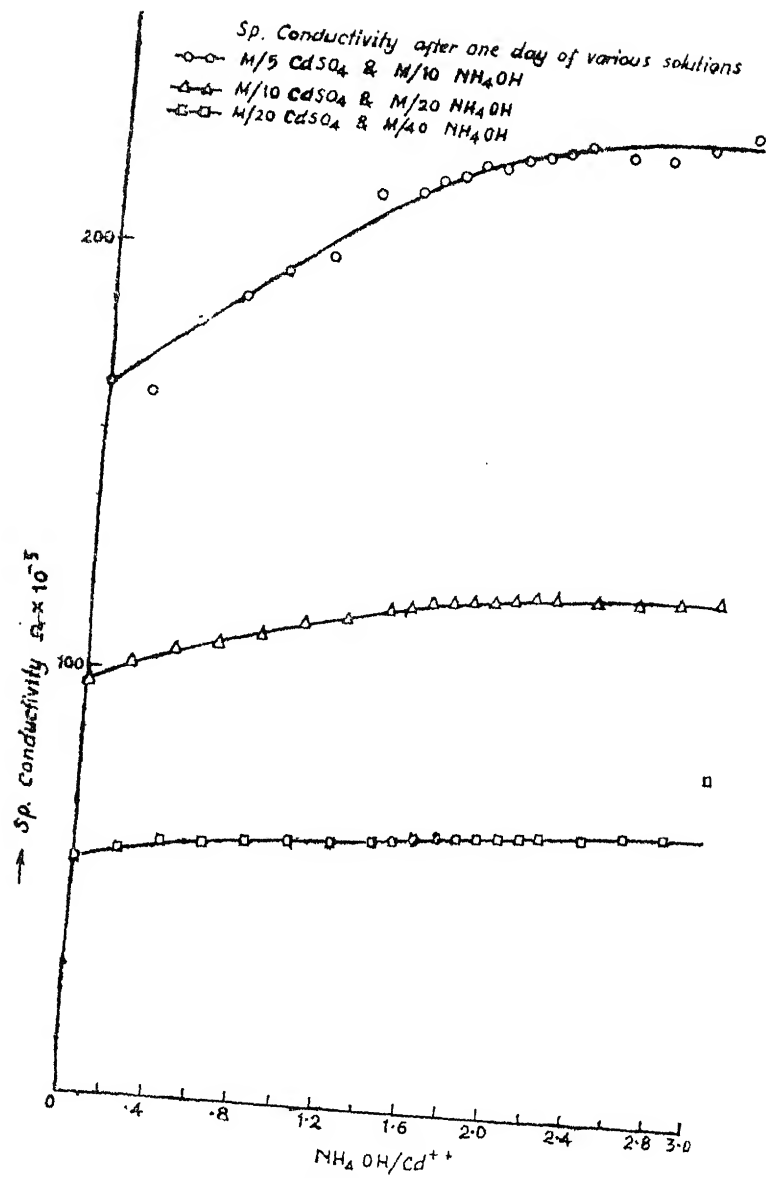


Fig. 5

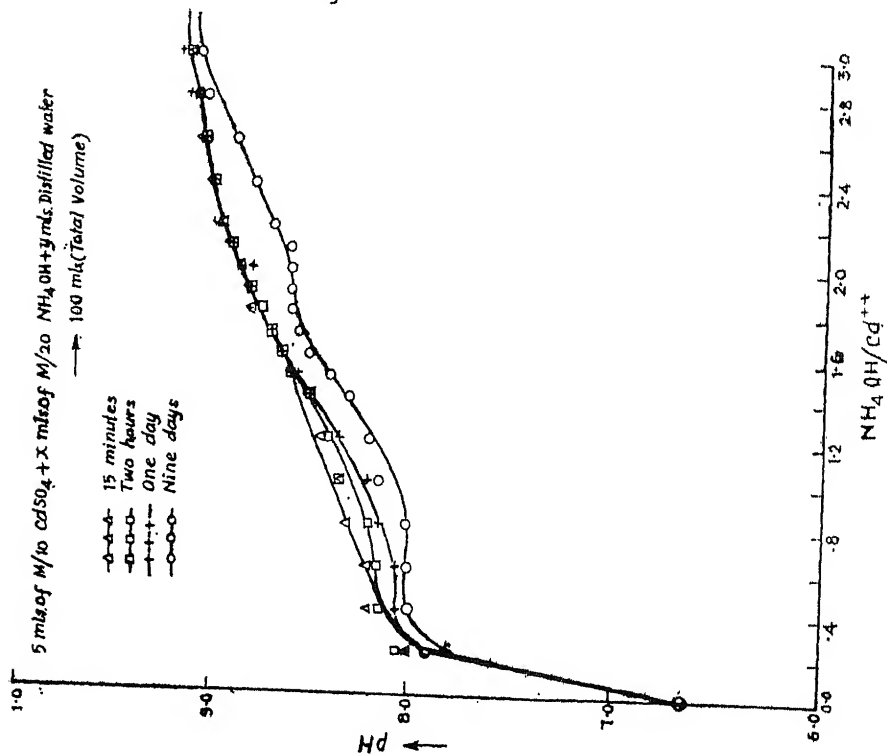


Fig. 6

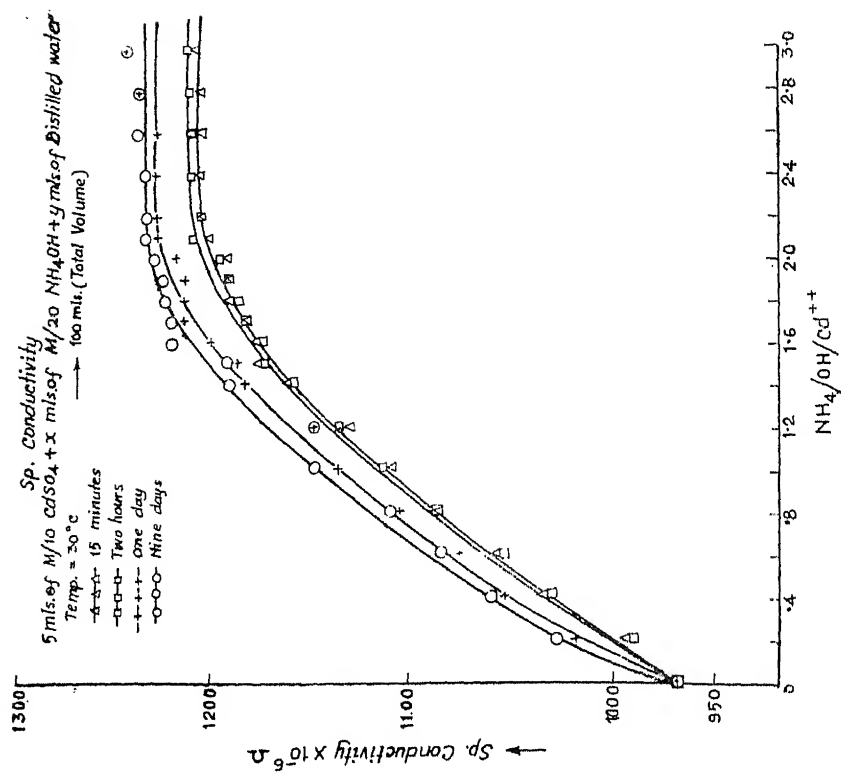


Fig. 7

Discussion

Precipitation Studies.

From the Figs. 1 and 2, it is quite clear that cadmium cannot be completely precipitated by the addition of ammonium hydroxide, as much as about 1/5th of cadmium remains unprecipitated. With the progressive addition of ammonium hydroxide initially the amount of cadmium precipitated goes on increasing, attains a maximum value at a $\text{Cd}^{++} : \text{NH}_4\text{OH}$ ratio of approximately 1 : 1.6 and then tends to be constant, even though about 1/5th of cadmium still remains unprecipitated. It is due to the formation of cadmium tetramine complex² with excess of ammonium hydroxide. It is further confirmed by a comparison of the curves in Figs. 1 and 3, which reveal that on adding ammonium hydroxide to a cadmium sulphate solution, initially much more of cadmium is precipitated, but later on some of it slowly passes into solution owing to the formation of the complex.

Similarly the amount of sulphate associated with the precipitate also goes on increasing with the progressive addition of ammonium hydroxide and attains a maximum value at almost the same $\text{Cd}^{++} : \text{NH}_4\text{OH}$ ratio of 1 : 1.6 (Figs. 1 and 2). But after that the curve falls, and then tends to be constant. In Fig. 3 (time of contact 15 minutes) however, the maximum value of associated sulphate is observed at a $\text{Cd}^{++} : \text{NH}_4\text{OH}$ ratio 1 : 1.25, a region, in which a break occurs in the curve of precipitated cadmium as well. Further a comparison of the curves in Figs. 1 and 3 indicates that the amount of associated sulphate ion in first fifteen minutes is less than that obtained after one day. It may be due to the adsorption of SO_4^{--} by the precipitate. But from Fig. 3 it is also evident that some amount of associated SO_4^{--} is retained even after thorough washing, which means that along with adsorption some sulphate is also present in the combined state, *i.e.*, some hydroxy sulphates are also being precipitated.

Fig. 4 contains the pH titration curves of cadmium sulphate by ammonium hydroxide at three different concentrations. With the progressive addition of ammonium hydroxide the curves rise and then tend to be constant. Similar is the behaviour of the conductance curves in Fig. 5. Thus these curves resemble the curves of titration of a weak acid and a weak base. Precipitation of cadmium hydrous oxide starts right from the very beginning as the pH values of all the solutions lie above pH 7, in the alkaline range.

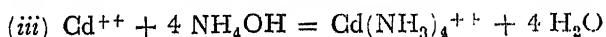
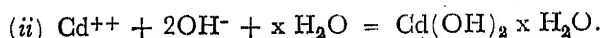
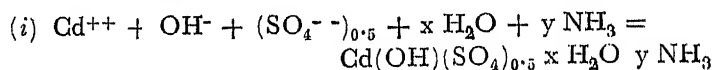
TABLE 1
(Based on Fig. 3)

Amount of mixed NH_4OH $\text{Cd}^{++} : \text{NH}_4\text{OH}$	$\text{OH}^-/\text{Cd}^{++}$	$\text{SO}_4^{--}/\text{Cd}^{++}$
1 : 0.25	1.19	.10
: 0.50	0.96	.06
: 0.75	1.05	.05
: 1.00	1.28	.09
: 1.25	1.56	.12
: 1.50	1.63	.09
: 1.75	1.87	.03

In the above table, $\text{Cd}^{++} : \text{OH}^-$ and $\text{Cd}^{++} : \text{SO}_4^{--}$ ratios have been calculated in the washed samples of hydrous cadmium oxide precipitates, the calculations being based on the results of Fig. 3. This shows that upto 0.75 equivalents of ammonium hydroxide added $\text{Cd}^{++} : \text{OH}^-$ ratio is nearly equal to 1:1, but afterwards it goes on increasing, the probable ratios being 1:1.33, 1.50, 1.66 etc. Thus here is an evidence of the precipitation of $\text{Cd}(\text{OH})(\text{SO}_4)_{\frac{1}{2}}$ as well, when cadmium is precipitated by ammonium hydroxide (also see Fig. 3). It is also quite probable that this precipitate may be having some ammonia molecules as ammonia of crystallization, and may be represented by a formula $\text{Cd}(\text{OH})(\text{SO}_4)_{\frac{1}{2}} \times \text{H}_2\text{O} \cdot y\text{NH}_3$, simple $\text{Cd}(\text{OH})(\text{SO}_4)_{0.5} \times \text{H}_2\text{O}$ being a soluble variety.³ But again according to this formula the $\text{Cd}^{++} : \text{SO}_4^{--}$ ratio should be 1:0.5, whereas the results indicate that this ratio is much less. This may be explained to be due to the mixed precipitation of hydroxy sulphato and pure hydroxy complexes, as suggested earlier.

With further progressive addition of ammonium hydroxide $\text{Cd}^{++} : \text{OH}^-$ ratios in the precipitates go on increasing, suggesting that various hydroxy sulphato and hydroxy complexes with increasing OH contents are successively precipitated, finally resulting into cadmium hydroxide. At the same time the results are also influenced by the formation of amine complex, so that an appreciable quantity of cadmium is left in solution.

Thus the various reactions occurring during interaction of cadmium sulphate and ammonium hydroxide may be represented by the following equations :



Studies on Ageing.

From the pH curves in Fig. 6, it is quite clear that with increasing age of the precipitates H^+ are released in the system. It is also confirmed by the conductance curves in Fig. 7, as with increasing age the solutions are becoming more conducting. Thus this supports the theory of ololation and oxolation taking place during the process of ageing as suggested earlier.

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Studies in Ageing of Hydrrous Cadmium Oxide : Effect on the Adsorption of Dichromate Ions, Congo Red and Alizarin Red-S Dyes

By

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[Received on 13th December, 1966]

Abstract

It is observed that the adsorption of $Cr_2O_7^{--}$, congo red and alizarin red-S dyes decreases with increasing age of the hydrrous cadmium oxide samples. Further the amount of adsorption decreases in the order $A > B > C$ in the case of $Cr_2O_7^{--}$, but increases in the case of congo red and alizarin red-S dyes in the order $A < B < C$. It has been suggested that the adsorption of dye anions occurs through the exchange of hydroxyl ions present at the surface of the hydrrous oxide.

Introduction

The adsorptive capacity of hydrrous oxides¹ is well known to decrease with ageing. Tewari, Dey and Ghosh² discussed the mechanism of ageing of hydrrous oxides and attributed the decrease in the surface activity to the growth and agglomeration of minute particles into bigger aggregates. Lottermoser³, by his sedimentation experiments and X-ray studies, has also obtained during ageing an evidence of the growth of particles and the orientation of structural units of smaller particles. According to Thomas⁴, the hydrrous oxides may slowly lose water molecules through olation, followed by oxolation so that bigger chemically inert polymeric aggregates are formed with ageing. In the present paper the adsorption of dichromate ions, Congo Red and Alizarin Red-S dyes on different samples of hydrrous cadmium oxide aged for different periods has been studied to demonstrate that the surface activity of the samples decreases with ageing.

Experimental

Three samples *A*, *B* and *C* of hydrrous cadmium oxide were prepared by precipitating cadmium by different quantities (20% deficient, equivalent, and 20% excess) of sodium hydroxide from a cadmium sulphate solution and thoroughly washed till free from ions. The pH values of the three samples were noted and found to be 8.5, 8.8 and 9.0, respectively for samples *A*, *B* and *C*. The amounts of CdO in 5 mls. of the suspension of the three samples were checked by estimating Cd^{++} at the time of experimentation.

Adsorption of $Cr_2O_7^{--}$:—5 mls. of the suspension were taken in each of a set of boiling tubes. In another set of boiling tubes different volumes (5, 10, 15, 20, 25 and 30 mls.) of a $N/20$ solution of potassium dichromate were taken and raised to 35 mls. in each case. Then the suspension and potassium dichromate solutions were well mixed (the total volume thus becoming 40 mls.), corked and left overnight. Next day the supernatant solutions were centrifuged and in a measured volume (5 mls.) of the clear solution $Cr_2O_7^{--}$ was estimated in each case by iodometric method. From the results obtained, the end concentration, the amount of $Cr_2O_7^{--}$ adsorbed and x/m ratios were calculated.

Similar experiments were performed with all the three samples aged for different periods. The results are graphically represented in the Figs. 1, 2 and 3 in which x/m ratios are plotted against residual concentrations of $Cr_2O_7^{--}$.

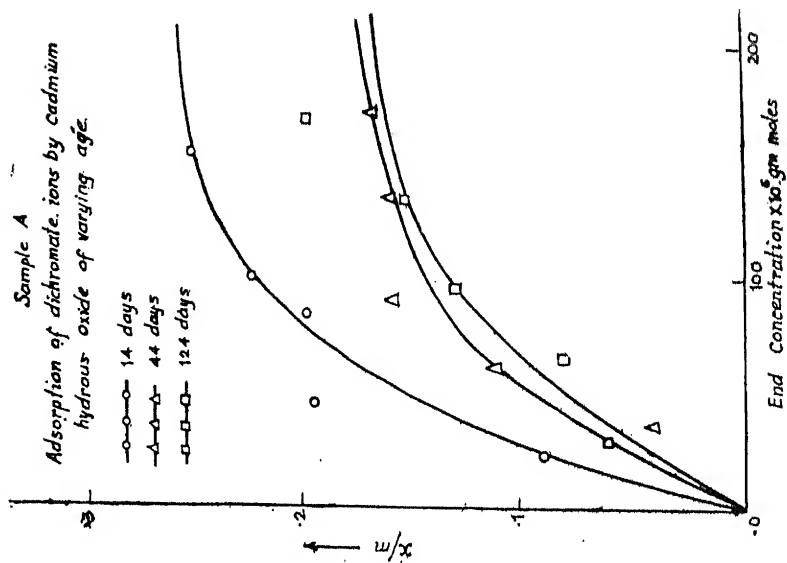


Fig. 1

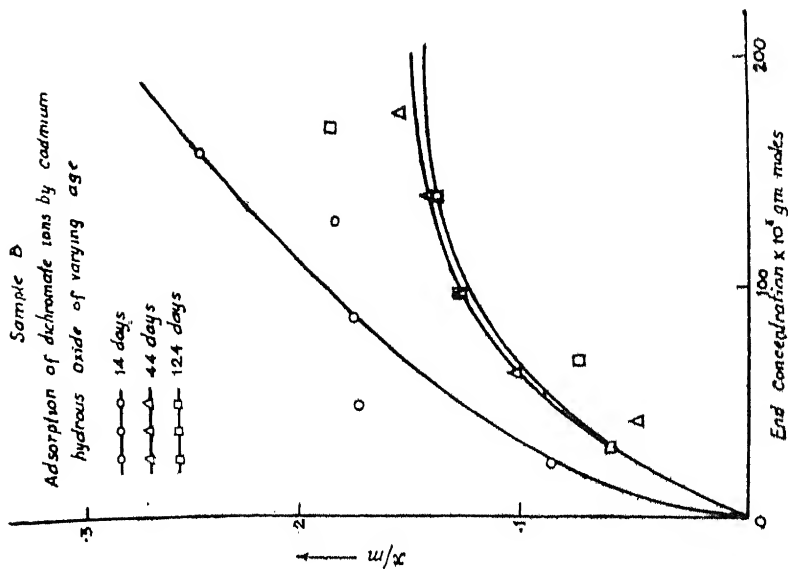


Fig. 2

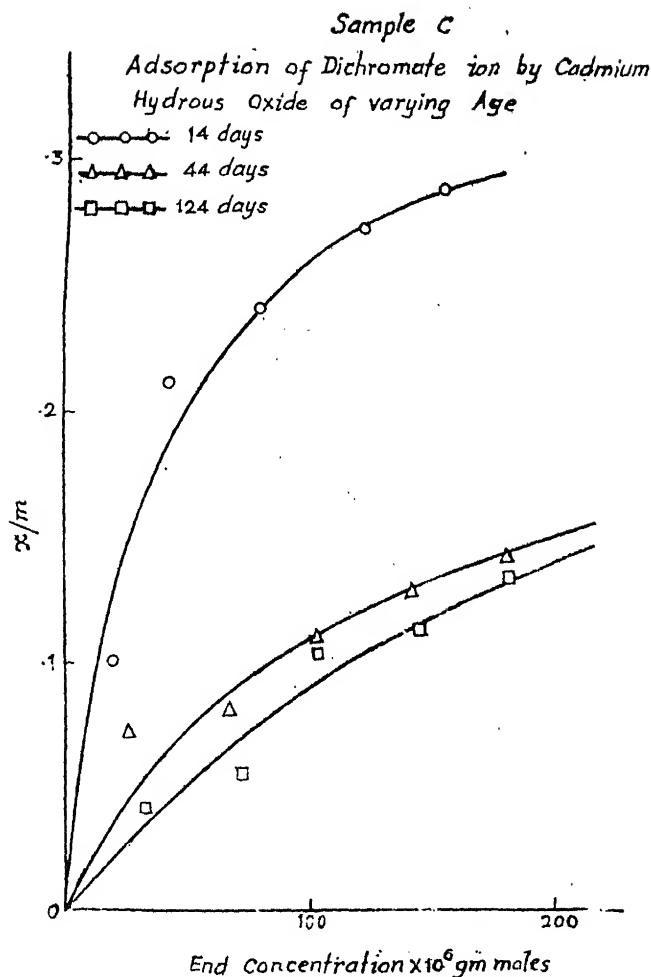


Fig 3

Adsorption of Dyes :—Similar experiments for the adsorption studies of dyes on the three samples were performed. The residual dye concentrations have been measured in the centrifigates by Klett Summerson colorimeter in presence of an ammonium chloride-ammonia buffer of pH8. The addition of buffer was found necessary to maintain pH constant, because pH has an important bearing on the intensity of the colour of dye solutions.

A calibration curve was drawn between the colorimeter readings and dye concentration, and the residual concentrations of the dye left after adsorption have been calculated from this calibration curve. From these, the amounts of adsorbed dye and x/m ratios were calculated. The results are given in Figs. 4 to 9, in which x/m ratios have been plotted against residual dye concentrations.

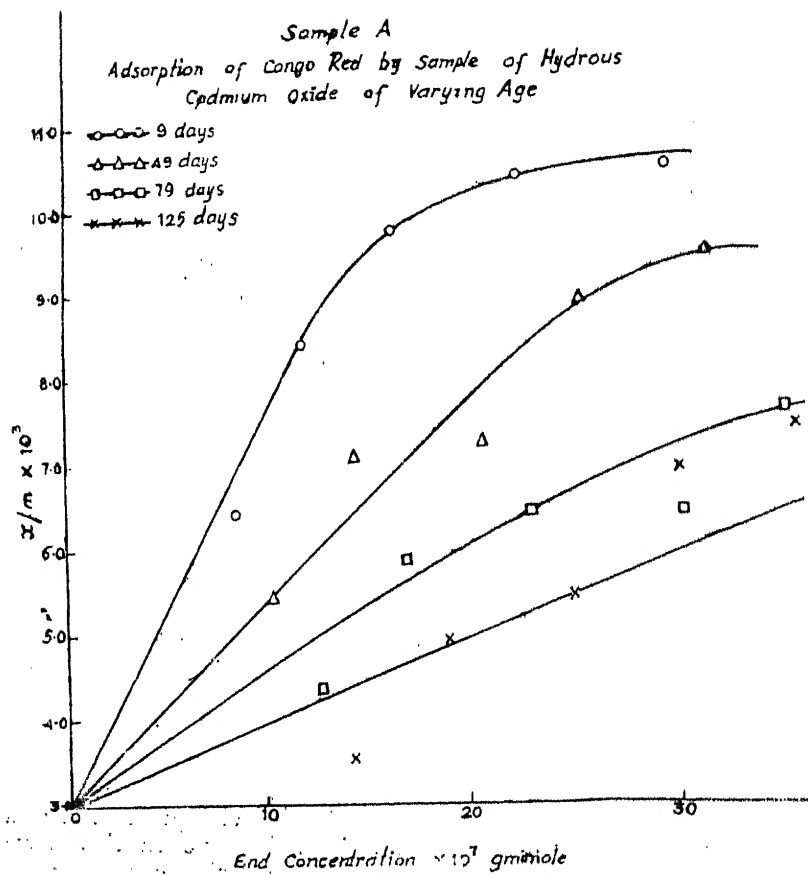


Fig. 4

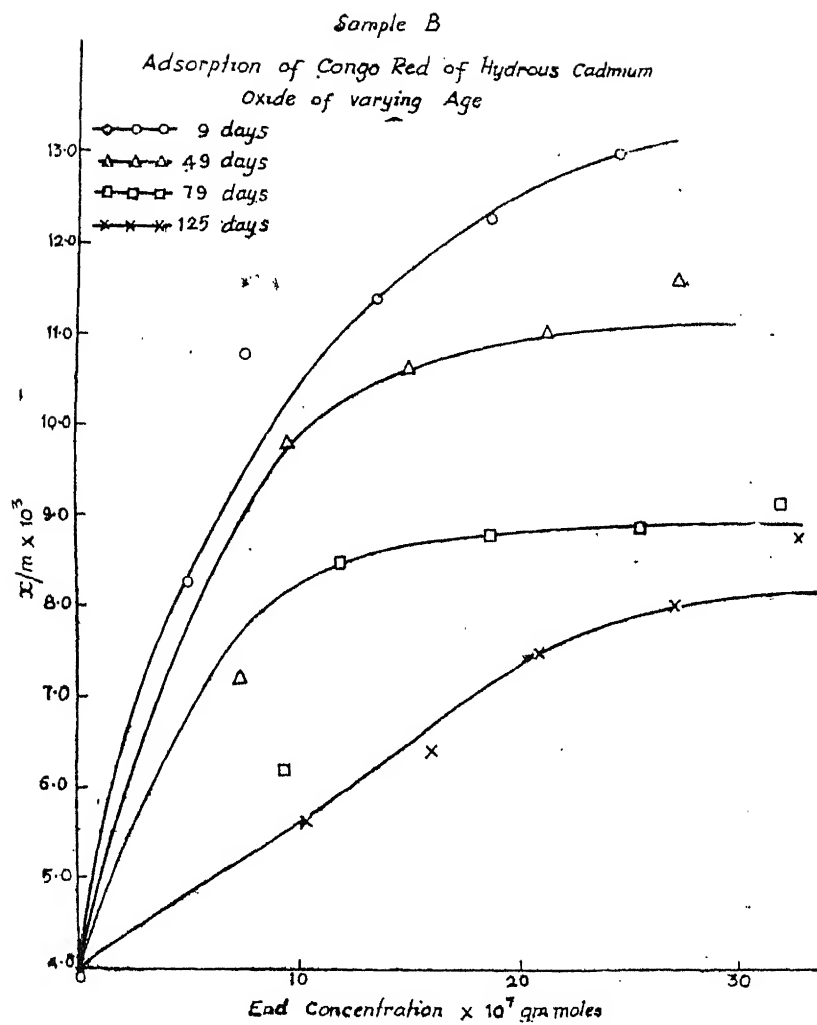


Fig. 5

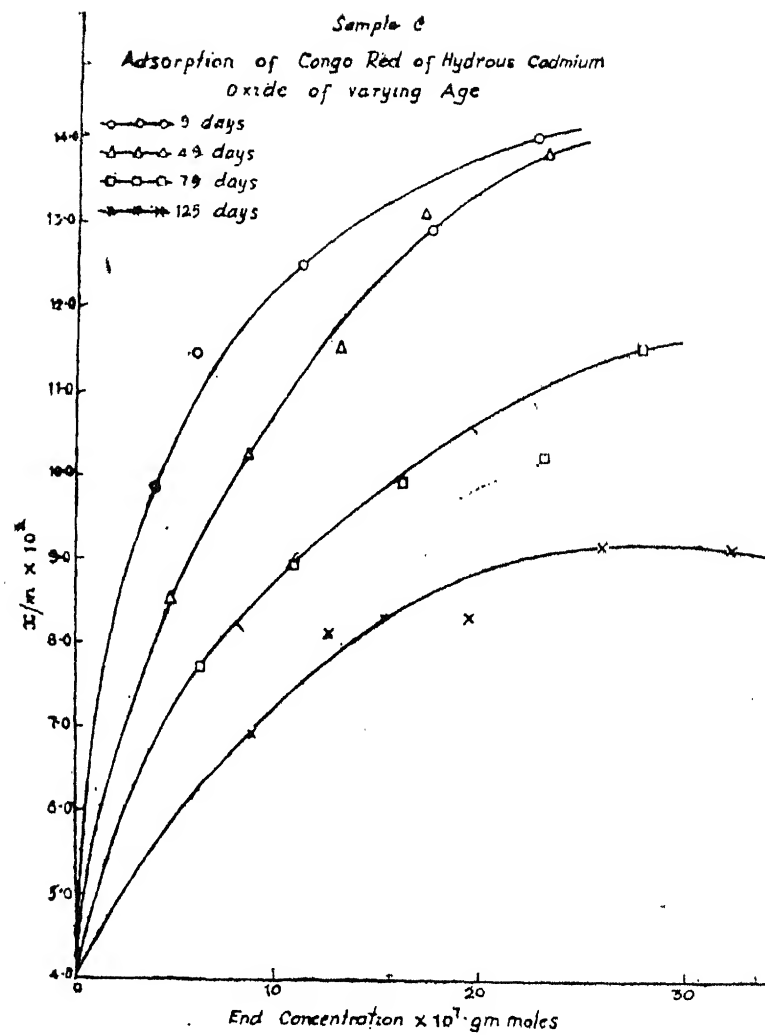


Fig. 6

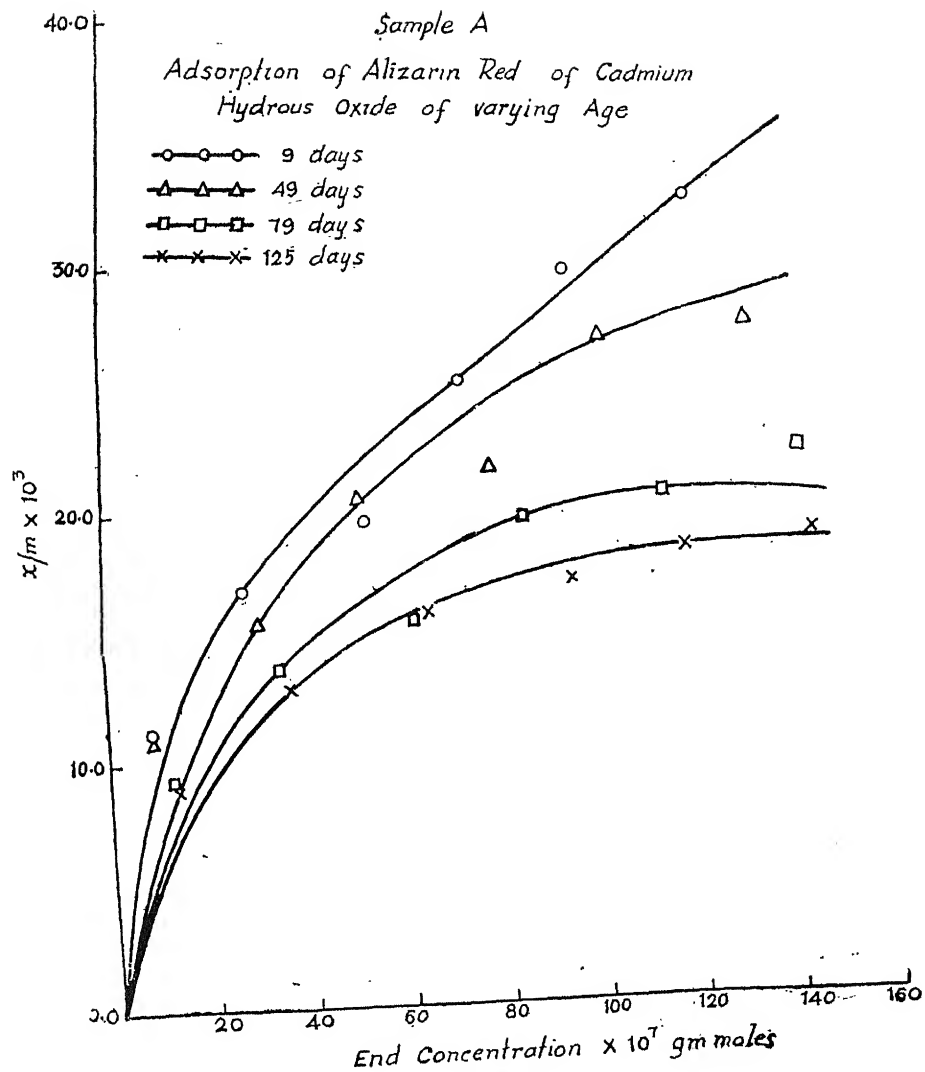


Fig. 7

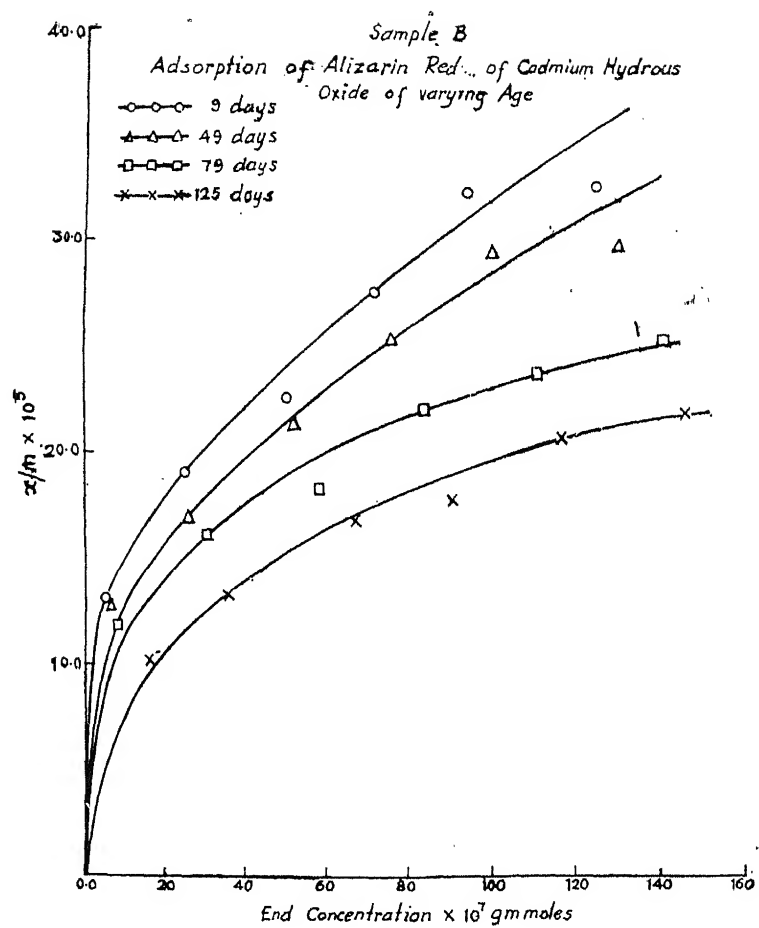


Fig. 8

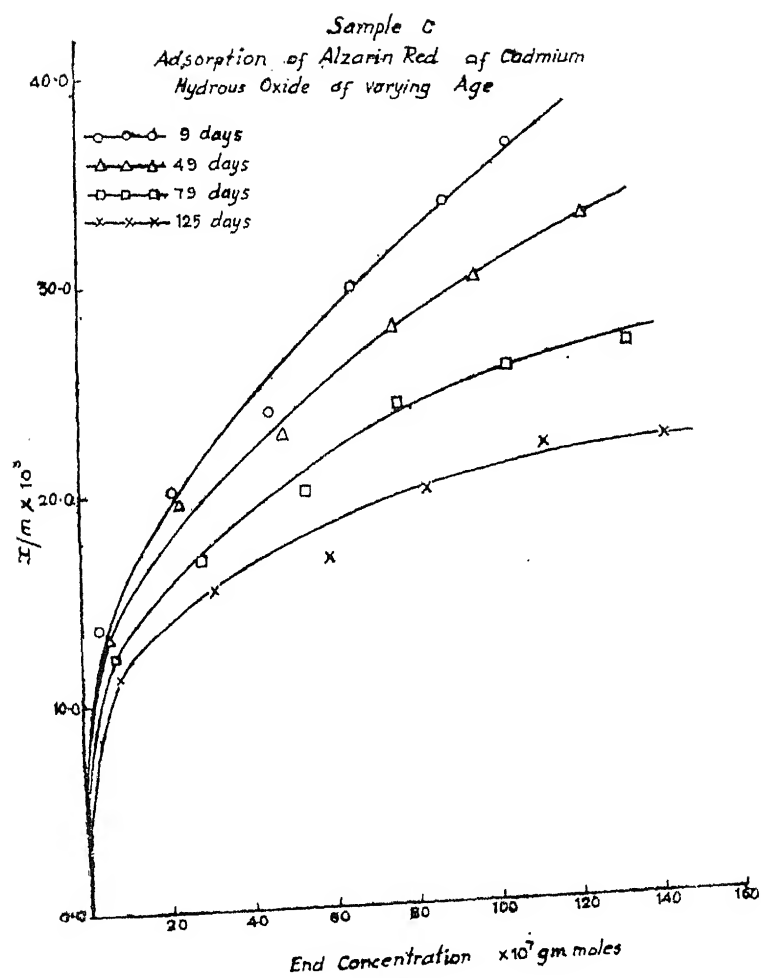
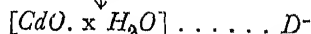
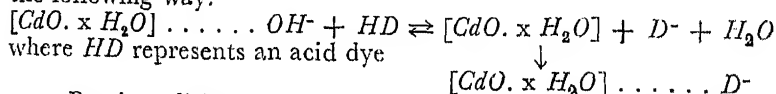


Fig. 9

Discussion

The results on the adsorption of $Cr_2O_7^{2-}$ by the three samples of hydrous cadmium oxide *A*, *B* and *C* aged for different periods are given in Figs. 1, 2 and 3. The results indicate that there is a marked decrease in the adsorption of $Cr_2O_7^{2-}$ with ageing in all the samples. This decrease is much pronounced up to 44 days, but after that there is rather little difference. Further a comparison of the results will show that except for the readings of 14 days, the amounts adsorbed by the three samples decrease in the following order $A > B > C$, indicating that the samples become more negative as the amount of the alkali added for precipitation is increased. This is substantiated by the pH values of the three samples ($A = 8.5$, $B = 8.8$ and $C = 9.0$). In 14 days samples, however, the amounts of adsorption are nearly the same in samples *A* and *B* (Sample *A* being slightly greater than *B*), but in sample *C* the amount adsorbed is definitely larger. It is probably due to the fact that with increasing amounts of alkali (beyond nearly 1.5 equivalents) added, the precipitates become finer, whereas in the sample *A* the precipitate is more or less flocculent⁶. Therefore, in the comparatively fresh samples, the surface may be larger in sample *C* than in sample *A* and this factor out-does the positive or negative natures of the two samples *A* and *C*. One more interesting feature of the curves in Figs. 1, 2 and 3 is that they are concave to the concentration axis, resembling the one obtained in the adsorption of nitrogen⁶ on charcoal (at 183°C).

Figs. 4 to 9 deal with the adsorption studies with congo red and alizarin red-S dyes. These also show a marked decrease in the adsorptive capacity of all the three samples with ageing. But here, there is a continuous fall in the amounts adsorbed with the increasing age of the precipitates. Further a comparison of the results indicates that with these dyes the adsorption increases in the following order $A < B < C$, an order reverse to that obtained in the case of $Cr_2O_7^{2-}$. It so appears that these acid dyes are adsorbed on hydrous cadmium oxide precipitates in the form of dye anions, and hence the amount of dye adsorbed depends upon the availability of dyes in the form of anions. Sample *C*, having a higher pH value is able to dissociate these dyes to a greater extent, and hence adsorption is also more. The mechanism of adsorption may be represented in the following way.



But in a dichromate solution, the $Cr_2O_7^{2-}$ are already present in ionised state, and feel a force of repulsion from the OH^- present over the surface of cadmium hydrous oxide precipitate, this repulsion being largest in sample *C*, because of its higher alkalinity.

Further in Figs. 7 to 9 (pertaining to adsorption of Alizarin red-S) the curves are concave to the concentration axis as in the adsorption of $Cr_2O_7^{2-}$, but the curves in Figs. 4 to 6 (adsorption of congo red in samples *A* and *B*) tend to be somewhat convex to concentration axis, specially as the ageing proceeds. This indicates that in such cases some multilayered adsorption may also occur.

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Chemical Examination of the plant 'Fagonia cretica' Linn

Part—II

By

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[Received on 24th November, 1966]

Abstract

The water extract of the ethanolic residue obtained from the plant 'Fagonia cretica' Linn. has been shown to contain amino acids (arginine, glycine, leucine and asparagine), sugars (lactose, glucose, D-ribose and galacturonic acid) and a glucoside which on hydrolysis yielded β -sitosterol and glucose. The methanolic extract of the ethanolic residue insoluble in water and acetone yielded a saponin, m. p. 180-185°C, which on acid hydrolysis furnished oleanolic acid, glucose and galacturonic acid.

Introduction

'Fagonia cretica' Linn (N. O. *Zygophyllaceae*) is a small spiny under-shrub with stiff branches and is used in curing various diseases^{1,2}. In an earlier communication³ some of its chemical components have been reported. The ethanolic extract of the plant after removal of the fat was successively extracted with water, acetone and methanol. The results of the study of the products isolated from these extracts are reported in the present paper.

Procedure and Results

An extract of the dried and powdered plant material (5 kg) was prepared by refluxing it with ethanol for several hours. The extract on cooling and keeping overnight gave a deposit which was separated by filtration and was studied previously³. The filtrate was evaporated to dryness and a residue (yield 540 gm) was obtained. This ethanolic residue was treated with petroleum ether to remove fat. The remaining residue was treated with warm water and the water extract was evaporated when a residue (Fraction No. 1, yield 95 gm.) was obtained. The water insoluble ethanolic residue was then extracted with acetone and the acetone extract (Fraction No. 2) was obtained by filtration. To the remaining ethanolic residue (200 gm.) a small amount of warm methanol was added. The mixture was shaken and filtered. This process was repeated several times. All the filtrates were mixed up and the methanolic extract thus obtained was treated with ether and a precipitate obtained. The precipitate was redissolved in methanol and reprecipitated with ether. This process was repeated several times till a brown sticky mass (Fraction No. 3, yield 10.5 gm.) was obtained.

Fraction No. 1.

(a) A small portion (0.3 gm.) of it was redissolved in water and centrifuged. The clear solution was decanted and the amino acids present in it were identified by employing ascending paper chromatographic technique using *n*-butanol-acetic acid-water (4:1:5) mixture⁴ as solvent and ninhydrin as spray reagent. The examination revealed the presence of arginine, glycine, leucine and asparagine.

(b) The remaining portion of the Fraction No. 1 was dissolved in warm ethanol and concentrated to about 200 ml. Equal amount of water was added to it. To this was then added a solution of lead acetate, when a precipitate (lead-lake) was obtained. The precipitate was filtered and this (lead-lake), as well as, the filtrate was studied.

(i) *Lead-lake*.—The lead-lake was suspended in alcohol, H_2S passed into it and filtered. The filtrate was boiled to remove H_2S and concentrated. The concentrated liquor thus obtained was hydrolysed with 2 N sulphuric acid when an insoluble mass appeared and was then filtered. The filtrate was shaken with barium carbonate to neutralise the acid, and the precipitated barium sulphate and the excess barium carbonate were filtered off. The filtrate was found to contain glucose when subjected to paper chromatographic analysis.

The insoluble mass which was obtained by hydrolysing the concentrated liquor as given above was found to be phenolic in nature and it showed properties similar to the colouring matter obtained from the Fraction No. 2 described later.

(ii) *Filtrate*.—The filtrate was treated with strong ammonia solution. A precipitate appeared which was filtered. The precipitate and the filtrate were examined as follows :—

(a) *Precipitate*.—It was suspended in alcohol, H_2S passed into it, and the precipitate removed by filtration. The filtrate was then evaporated to dryness to give solid residue. It gave the tests of glucosides and was hydrolysed with 2 N sulphuric acid. The hydrolysate was examined by paper chromatography and was found to contain glucose. The aglycon was recrystallised from methanol when a pure crystalline compound, m.p. $135-136^\circ C$ was obtained. This compound underwent Liebermann-Burchard reaction for sterols and was identified as β -sitosterol.

(b) *Filtrate*.—The lead present in the filtrate was removed by passing hydrogen sulphide into it and filtering off the precipitated lead sulphide. The filtrate was concentrated to about 100 ml. and centrifuged. The clear solution obtained was evaporated when a sticky residue was left. This residue reduced Fehling's as well as ammonical silver nitrate solutions showing that it contained reducing sugars.

Characterization of Reducing sugars by paper chromatography

Ascending paper chromatographic technique, using Whatman No. 1 filter paper (sheet 24×12 cm.) and *n*-butanol-acetic acid-water (4:1:5) as solvent, was employed. The sugar solution together with reference sugars (Reagent grade) was chromatographed at room temperature for twelve hours. The developed chromatograms were sprayed with a solution of aniline hydrogen phthalate. The spots located by heating the chromatogram in an electric oven at $120^\circ C$ for one hour revealed the presence of lactose, glucose, D-ribose and galacturonic acid.

The presence of the sugars mentioned above was also confirmed by preparing their suitable derivatives. Ten chromatograms (48×36 cm.) were run for 24 hours and horizontal strips each containing one sugar spot were cut, which was done by comparing and measuring the distances according to the sprayed and identified chromatogram. The corresponding ten strips of each sugar were eluted with warm distilled water. The eluates were concentrated separately and suitable derivatives (*viz.*, oxime, osazone) of each sugar were prepared and identified.

Fraction No. 2

The acetone extract was precipitated with ether and filtered. The precipitate was redissolved in acetone and reprecipitated by ether. The precipitate was dried when an amorphous black powder (yield 3.5 gm.) was obtained. All attempts to crystallise this compound were unsuccessful. This amorphous product melted at 115-120°C and was soluble in acetone, ethyl acetate, sodium hydroxide and partially in water. With concentrated hydrochloric and nitric acids it gave brown coloration. With alcoholic ferric chloride it gave green coloration indicating the presence of phenolic (-OH) group. Ethanolic solution of the compound gave yellow precipitate with neutral lead acetate solution. An orange to red coloration was obtained on treating with Mg/HCl, while Zn/HCl and sodium acetate had no effect and the original yellow colour of the solution persisted. On the basis of the above observations it was concluded that the compound belongs probably to the flavonoid⁵ group of colouring matter, but nothing about its structure could so far been pursued due to its non-crystalline nature. Attempts are being made to get this compound in pure crystalline form.

Fraction No. 3

The brown sticky residue was dried in vacuum over calcium chloride when an amorphous and hygroscopic powder, m.p. 165-171°C was obtained. This was purified several times from ethanol when a cream coloured amorphous hygroscopic compound, m. p. 180-185°C, was obtained. An aqueous solution of this compound on shaking formed characteristic soapy foam indicating it to be a saponin⁶. Only one spot was observed during its paper chromatography using *n*-butanol-acetic acid-water (4:1:5v/v) as solvent and 5% tri-chloroacetic acid in ether as spraying reagent⁷.

The saponin was hydrolysed by heating it with 4N sulphuric acid on a water bath for 16 hours. A little ethanol was added to the reaction mixture at intervals to reduce frothing. The white precipitate of sapogenin was separated from the hydrolysate by filtration.

Study of sapogenin

The acid sapogenin was crystallised several times from ethanol. Further purification was achieved by dissolving the sapogenin in about 10% sodium hydroxide solution followed by decomposition of the sodium salt thus obtained with hydrochloric acid. The product obtained on crystallisation from methanol yielded fine needles, m. p. 299-301°C.

Found	Calculated for
C = 78.18% H = 10.48%	C ₃₀ H ₄₈ O ₃
Mol. wt. = 464	C = 78.94%, H = 10.52%
(Semi-micro Rast)	Mol. wt. = 456

The sapogenin thus has the molecular formula C₃₀ H₄₈ O₃. It gave a purple colour with thionyl chloride (Noller's reaction), a red violet colour with acetic anhydride and concentrated sulphuric acid (Liebermann-Burchard reaction), and yellow colour with tetranitromethane showing that it was a triterpene⁸. On

heating with acetic anhydride and pyridine it furnished an acetate which was crystallised from methanol whereby white needles (m.p. 262–264°C.) were obtained.

Identification of sugars in saponin hydrolysate

The hydrolysate was shaken with barium carbonate to neutralise the acid. The precipitated barium sulphate and excess of barium carbonate were filtered off, and washed with hot water. The washings were mixed with the filtrate and this solution (100 ml.) was concentrated to 50 ml. under reduced pressure. The hydrolysate was chromatographed on Whatman No. 1 filter paper using *n*-butanol-acetic acid-water mixture (4:1:5 v/v) as solvent employing ascending paper chromatographic technique. Two spots were located on spraying the developed chromatogram with aniline hydrogen phthalate and heating it in an electric oven at 120°C. The R_F values of the spots revealed the presence of glucose and galacturonic acid. This was also confirmed by running a chromatogram of saponin hydrolysate together with reference sugars (reagent grade).

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Precipitation of Hydrus Cadmium Oxide—III Influence of different Anions on the Precipitation of Hydrus Cadmium Oxide in CdSO_4 -NaOH System

By

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Abstract

It is observed that the precipitation of hydrus cadmium oxide is influenced by the presence of other anions. The pH at which the precipitation starts, increases in the presence of neutral salts, which is probably due to the formation of anionic complexes like CdX_4^{--} , the increase being in the order of $\text{Cl}^- < \text{Br}^- < \text{I}^-$. The ratios of $\text{Cd}^{++} : \text{OH}^-$ at which the pH curves became vertical were also noted, the values being (Blank 1.50), K_2SO_4 (1.50), KCl (1.33) KBr 1.40 and KI (1.45).

Introduction

In previous publications^{1,2} from this laboratory results were reported on the precipitation studies of hydrus cadmium oxide from a solution of cadmium sulphate by the addition of sodium hydroxide and ammonium hydroxide. In this paper the influence of various anions on the precipitation of hydrus cadmium oxide by sodium hydroxide has been studied.

Experimental

Varying volumes of a standard caustic soda solution were added to 10 mls. of 0.1 M CdSO_4 solution in different 100 mls. volumetric flasks, both in the absence and presence of a fixed volume (10 mls.) of 0.2M solutions of potassium sulphate, potassium chloride, potassium bromide and potassium iodide. Next day in the centrifugates cadmium was estimated as done earlier, and the results are given in Fig. 1.

The pH of the above reaction mixtures was also measured by a Leeds Northrup pH meter. The results are shown graphically in Fig. 1.

Discussion

From the results it is clear that the precipitation of hydrus cadmium oxide is some what influenced by the presence of other alkali salts. In general, the pH at which the precipitation starts increases in the presence of salts, but this increase is not so much as reported by Vinogradova³. These slight changes may be due to the formation of anionic complexes like $(\text{CdX}_4)^{--}$. From the pH curves it is clear that this increase in the case of halides is in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$ which is parallel to the order of their stability constants⁴.

It is further observed that the amounts of cadmium precipitated also increase in the presence of added salts. The pH curves become vertical at the following $\text{Cd}^{++} : \text{OH}^-$ ratios in different conditions.

Blank (CdSO_4 alone)	1.50
K_2SO_4	1.50
KCl	1.33
KBr	1.40
KI	1.45

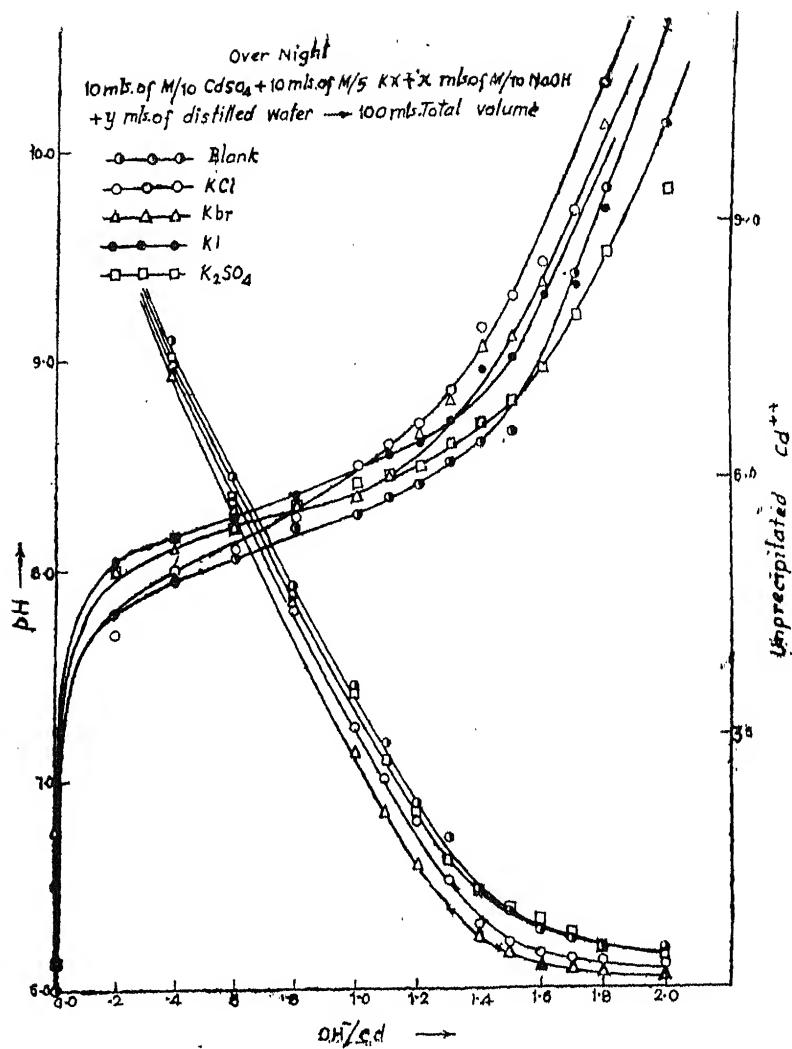


Fig. 1

These values are, in general, in agreement with those reported by Moeller⁵. This decrease in the value of $\text{Cd}^{++} : \text{OH}^-$ ratios in the presence of added halides may be due to the precipitation of some hydroxy halides as well, so that precipitation is completed earlier. Another explanation of such a phenomenon may be found in the adsorption⁶ of these ions releasing some free alkali, which may further precipitate cadmium, but in that case the ratio must have been suppressed by potassium sulphate as well.

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Certain integral equations and Self-reciprocal functions

By

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1. Introduction

A generalisation of the Hankel transform

$$(1.1) \quad g(x) = \int_0^\infty \sqrt{xy} J_\nu(xy) f(y) dy$$

has been introduced by R. Narain [3, p. 270] in the form

$$(1.2) \quad g(x) = 2^{-\nu} \int_0^\infty (xy)^{\nu+1} \chi_{\nu,k,m} \left(\frac{x^2 y^2}{4} \right) f(y) dy$$

where

$$\chi_{\nu,k,m}(x) = x^{-\nu} G \begin{matrix} 2, 1 \\ 2, 4 \end{matrix} \left[x \left| \begin{matrix} k-m-\frac{1}{2}, \nu-k+m+\frac{1}{2} \\ \nu, \nu+2m, -2m, 0 \end{matrix} \right. \right]$$

He calls $g(x)$ in (1.2) to be $\chi_{\nu,k,m}$ -transform of $f(x)$ and has proved in the same paper that this is a transform reciprocal like the Hankel transform. In case $g(x) \equiv f(x)$, we may call it to be self-reciprocal in the $\chi_{\nu,k,m}$ -transform and we shall say that $f(x)$ is $R_\nu(k, m)$.

When $k+m = \frac{1}{2}$, (1.2) reduces to (1.1).

In this paper, we have investigated the integral equations satisfied by the infinite series:

$$(1.3) \quad f(x) + f(2x) + f(3x) + \dots$$

and

$$(1.4) \quad f(x) - f(x) + f(5x) - \dots$$

when the function $f(x)$ is self-reciprocal under $\chi_{\nu,k,m}$ -transform. We have also found certain functions which play the roles of transforms and that the series of the types (1.3) and (1.4) are self-reciprocal under some of the new transforms.

2. Theorem 1

If $f(x)$ is $R_\nu(k, m)$, then the function defined by

$$F(x) = \sum_{r=1}^{\infty} f(rx),$$

satisfies the integral equation

$$(2.1) \quad \frac{1}{2} f(0) + F(x) = \frac{\phi(1)}{x} + \int_0^\infty \psi_\nu(xy) F(y) dy$$

where

$$\psi_\nu(x) = \frac{1}{\pi} \int_0^\infty X_\nu\left(\frac{xt}{2\pi}\right) \cos t \, dt$$

and

$$(2.2) \quad X_\nu(x) \equiv \sqrt{2} \, G_{2,4}^{2,1} \left[\frac{x^2}{4} \left| \begin{matrix} k-m-\frac{\nu}{2}-\frac{1}{4}, -k+m+\frac{\nu}{2}+\frac{3}{4} \\ \frac{\nu}{2}+\frac{1}{4}, \frac{\nu}{2}+\frac{1}{4}+2m, \frac{1}{4}-\frac{\nu}{2}, \frac{1}{4}-\frac{\nu}{2}-2m \end{matrix} \right. \right]$$

and

$$\phi(s) = \int_0^\infty f(x) \cdot x^{s-1} \, dx$$

provided that

(i) $f(x)$ is continuous in $x \geq 0$,

(ii) $\sum_{r=1}^\infty f(rx)$ is uniformly convergent in the arbitrary interval $(0, a)$,

where a may be taken as large as we please, and

(iii) $\int_0^\infty |f(x)| \, dx$ is convergent.

Proof

It is easy to see that $\psi_\nu(x)$, defined above is continuous and bounded in $(0, \infty)$, $\operatorname{Re}(\nu + \frac{1}{2} + 2m \pm 2m) > 0$, $\operatorname{Re}(\nu + \frac{3}{2} + 2m - 2k) > 0$.

Let us consider the integral

$$I \equiv \int_0^\infty \psi_\nu(xy) F(y) \, dy \equiv \int_0^\infty \psi_\nu(xy) \sum_{r=1}^\infty f(ry) \, dy$$

Here term by term integration is easily justifiable by virtue of the conditions of the theorem. Hence we get

$$\begin{aligned} I &= \frac{1}{\pi} \sum_{r=1}^\infty \int_0^\infty f(ry) \, dy \int_0^\infty X_\nu\left(\frac{xyt}{2\pi}\right) \cos t \, dt \\ &= \sum_{r=1}^\infty \frac{1}{\pi r} \int_0^\infty \cos t \, dt \int_0^\infty f(y) X_\nu\left(\frac{xyt}{2\pi r}\right) dy. \end{aligned}$$

The change in the order of integration being justifiable by taking the range of integration from δ to ∞ and ultimately making $\delta \rightarrow 0$, thus we get

$$\begin{aligned} I &= \sum_{r=1}^\infty \frac{1}{\pi r} \int_0^\infty \cos t \, f\left(\frac{xt}{2\pi r}\right) dt \quad [\text{Since } f(x) \text{ is } R_\nu(k, m)] \\ &= \frac{2}{x} \sum_{r=1}^\infty \int_0^\infty f(t) \cos\left(\frac{2\pi r t}{x}\right) dt \\ &= \frac{1}{2} f(0) + F(x) - 1/x \end{aligned}$$

{ by Poisson's formula [4, p. 60 (2.8.1)] }

$$= \frac{1}{2} f(0) + f(x) \frac{\phi(1)}{x},$$

which proves the theorem.

Theorem 2

If $f(x)$ is $R_\nu(k, m)$, then the function defined as :

$$P(x) = f(x) - f(3x) + f(5x) - \dots$$

satisfies the integral equation

$$(2.3) \quad P(x) = \int_0^x \phi_\nu(xy) P(y) dy$$

where

$$\phi_\nu(x) = \frac{2}{\pi} \int_0^\infty \chi_\nu \left(\frac{2xt}{\pi} \right) \sin t dt$$

and $\chi_\nu(x)$ is as defined in (2.2), provided that

(i) $f(x)$ is continuous in $x \geq 0$,

(ii) the series $f(x) - f(3x) + f(5x) - \dots$

is uniformly convergent in the arbitrary interval $(0, a)$, where a may be taken as large as we please and

(iii) $\int_0^\infty |f(x)| dx$ is convergent

Here it is easy to note that the function $\phi_\nu(x)$ is continuous and bounded in $(0, \infty)$, $Re(\nu + \frac{1}{2} + 2m \pm 2m) > 0$, $Re(\nu + \frac{3}{2} + 2m - 2k) > 0$.

The proof of this theorem follows if we proceed as in theorem 1 and using Poisson's formula for sine transform [4, p. 66 (2.11.1)].

The conditions of convergence can be relaxed to a certain extent.

The expressions for $\psi_\nu(x)$ and $\phi_\nu(x)$ in term of Meijer's G-function

By Mellin's Inversion formula [4, p. 54 (2.1.23)] we have

$$\begin{aligned} \psi_\nu(x) &= \frac{1}{\pi} \int_0^\infty \chi_\nu \left(\frac{xt}{2\pi} \right) \cos t dt \\ &= \frac{1}{\sqrt{2\pi}} - \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{\Gamma_* \left(\frac{\nu}{2} + \frac{1}{4} + \frac{s}{2} + m \pm m \right) \Gamma \left(\frac{\nu}{2} + \frac{3}{4} - \frac{s}{2} + m - k \right) \Gamma \left(\frac{1}{2} - \frac{s}{2} \right)}{\Gamma_* \left(\frac{\nu}{2} + \frac{3}{4} - \frac{s}{2} + m \pm m \right) \Gamma \left(\frac{\nu}{2} + \frac{3}{4} + \frac{s}{2} + m - k \right) \Gamma \left(\frac{s}{2} \right)} \\ &\quad \times \left(\frac{x}{2\pi} \right)^{-s} ds, \end{aligned}$$

using [1, p. 353 (43)], we get

$$(2.4) \quad \psi_\nu(x) = \frac{\sqrt{2}}{\pi} G_{4,4}^{2,2} \left[\frac{x^2}{4\pi^2} \left| \begin{matrix} -\frac{1}{4} - \frac{\nu}{2} - m + k, \frac{1}{2}, \frac{\nu}{2} + \frac{3}{4} + m - k, 0 \\ \frac{\nu}{2} + \frac{1}{4}, \frac{\nu}{2} + \frac{1}{4} + 2m, \frac{1}{4} - \frac{\nu}{2}, \frac{1}{4} - \frac{\nu}{2} - 2m \end{matrix} \right. \right]$$

So also

$$\begin{aligned} \phi_\nu(x) &= \frac{2}{\pi} \int_0^\infty x_\nu \left(\frac{2x}{\pi} t \right) \sin t \, dt \\ &= \frac{\sqrt{2}}{\sqrt{\pi}} \cdot \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{\Gamma_* \left(\frac{\nu}{2} + \frac{1}{4} + \frac{s}{2} + m \pm m \right) \Gamma \left(\frac{\nu}{2} + \frac{3}{4} - \frac{s}{2} + m - k \right) \Gamma \left(1 - \frac{s}{2} \right)}{\Gamma_* \left(\frac{\nu}{2} + \frac{3}{4} - \frac{s}{2} + m \pm m \right) \Gamma \left(\frac{\nu}{2} + \frac{3}{4} + \frac{s}{2} + m - k \right) \Gamma \left(\frac{1}{2} + \frac{s}{2} \right)} \\ &\quad \times \left(\frac{2x}{\pi} \right)^{-s} ds \\ (2.5) \quad \phi_\nu(x) &= \frac{2\sqrt{2}}{\sqrt{\pi}} G_{4,4}^{2,2} \left[\frac{4x^2}{\pi^2} \left| \begin{matrix} -\frac{1}{4} - \frac{\nu}{2} - m \pm k, 0, \frac{\nu}{2} + \frac{3}{4} + m - k, \frac{1}{2} \\ \frac{\nu}{2} + \frac{1}{4}, \frac{\nu}{2} + \frac{1}{4} + 2m, \frac{1}{4} - \frac{\nu}{2}, \frac{1}{4} - \frac{\nu}{2} - 2m \end{matrix} \right. \right] \end{aligned}$$

on using Mellin inversion formula.

Again by the theory of Mellin transform [4, p. 7 (1.5.1)], we have

$$\psi_\nu(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} R_1(s) x^{-s} ds,$$

where

$$R_1(s) = (2\pi)^{s-\frac{1}{2}} \frac{\Gamma_* \left(\frac{\nu}{2} + \frac{1}{4} + \frac{s}{2} + m \pm m \right) \Gamma \left(\frac{\nu}{2} + \frac{3}{4} - \frac{s}{2} + m - k \right) \Gamma \left(\frac{1}{2} - \frac{s}{2} \right)}{\Gamma_* \left(\frac{\nu}{2} + \frac{3}{4} - \frac{s}{2} + m \pm m \right) \Gamma \left(\frac{\nu}{2} + \frac{3}{4} + \frac{s}{2} + m - k \right) \Gamma(s/2)}$$

Here it is easy to see that $R_1(s)$ satisfies the equation

$$R_1(s) R_1(1-s) = 1$$

which at any rate, is a sufficient condition, in some sense, for $\psi_\nu(x)$ to play the role of a transform [4, p. 212-213 (§§ 8.1 and 8.2)].

As above we find that

$$\phi_\nu(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} R_2(s) x^{-s} ds,$$

where

$$R_2(s) = \frac{2^{1-s} \Gamma_* \left(\frac{\nu}{2} + \frac{1}{4} + \frac{s}{2} + m \pm m \right) \Gamma \left(\frac{\nu}{2} + \frac{3}{4} - \frac{s}{2} + m - k \right) \Gamma \left(1 - \frac{s}{2} \right)}{\pi^{1-s} \Gamma_* \left(\frac{\nu}{2} + \frac{3}{4} - \frac{s}{2} + m \pm m \right) \Gamma \left(\frac{\nu}{2} + \frac{3}{4} + \frac{s}{2} + m - k \right) \Gamma \left(\frac{1}{2} + \frac{s}{2} \right)}$$

We see that the function $R_2(s)$ also satisfies the relation

$$R_2(s) R_2(1-s) = 1,$$

which, in some sense, is a sufficient condition for $\phi_1(x)$ to play the role of a transform.

Further we find that $\psi_\nu(x)$ is the resultant kernel of the two kernels $\chi_\nu(x)$ and $\cos x$, each of which plays the role of transform; also $\phi_\nu(x)$ is the resultant of the kernels $\chi_\nu(x)$ and $\sin x$, and both of these play the role of transforms. Hence both the kernels $\psi_\nu(x)$ and $\phi_\nu(x)$ play the roles of transform [4, p. 229 (§ 8.11)].

We can also establish easily that

$$f(x) = \int_0^\infty \psi_\nu(xu) du \int_0^\infty \psi_\nu(ut) f(t) dt.$$

and

$$f(x) = \int_0^\infty \phi_\nu(xu) du \int_0^\infty \phi_\nu(ut) f(t) dt.$$

showing that $\psi_\nu(x)$ and $\phi_\nu(x)$ are two kernels which play the role of transforms.

If we look back to the theorem 2, we find that $P(x)$ is defined as

$$P(x) = f(x) - f(3x) + f(5x) - \dots$$

where $f(x)$ is $R_\nu(k, m)$ and the series on the right gives us a function which is self-reciprocal in $\phi_\nu(x)$ —transform.

We shall now construct theorems which are converse of the above theorems :

Theorem 3

If the series

$$f(x) + f(2x) + f(3x) + \dots$$

converges uniformly to $F(x)$, and if

$$\frac{1}{2} f(0) + F(x) = \frac{\phi(1)}{x} + \int_0^\infty \psi_\nu(xy) F(y) dy$$

where

$$\phi(s) = \int_0^\infty f(x) x^{s-1} dx$$

and $\psi_\nu(x)$ is as defined in the theorem 1, the function $f(x)$ is $R_\nu(k, m)$, provided that $f(x)$ is continuous and absolutely integrable in $(0, \infty)$.

Theorem 4

If the series

$$f(x) - f(3x) + f(5x) - \dots$$

converges uniformly to $P(x)$, and if

$$P(x) = \int_0^\infty P(y) \phi_\nu(xy) dy$$

where $\phi_\nu(x)$ is as defined in the theorem 2, then $f(x)$ is $R_\nu(k, m)$, provided that $f(x)$ is continuous and absolutely integrable in $(0, \infty)$

To prove these we shall require the following two results of Mainra [2, pp. 65-67].

Result I : If

$$(2.6) \quad \sum_{r=1}^{\infty} \int_0^{\infty} \cos(r x t) G(t) dt = 0$$

then $G(t) \equiv 0$,

provided that

(i) $G(t)$ is continuous and $O(t)$ when t is small.

(ii) $\int_0^{\infty} |G(t)| dt$ exists

and

(iii) $\sum_{r=1}^{\infty} \int_0^{\infty} \cos(r x t) G(t) dt$ is uniformly convergent.

Result II : Let $G(t)$ be continuous and absolutely integrable in $(0, \infty)$ and

$$\sum_{r=1}^{\infty} (-1)^{r+1} \int_0^{\infty} \sin(2r-1 xt) G(t) dt$$

be uniformly convergent. Further if

$$(2.7) \quad \sum_{r=1}^{\infty} (-1)^{r+1} \int_0^{\infty} \sin(2r-1 xt) G(t) dt = 0$$

then $G(t) \equiv 0$.

Now we shall prove the theorem 3 and 4 respectively. Let us consider the integral (for theorem 3)

$$\begin{aligned} I_1 &= \int_0^{\infty} \psi_\nu(xy) F(y) dy \\ &= \frac{1}{\pi} \sum_{r=1}^{\infty} \int_0^{\infty} \cos(rt) dt \int_0^{\infty} f(y) \chi_\nu\left(\frac{xyt}{2\pi}\right) dy, \end{aligned}$$

which we get after certain easily justifiable changes in the order of integration and summation.

Hence, we have

$$I_1 = \frac{1}{\pi} \sum_{r=1}^{\infty} \int_0^{\infty} G_2\left(\frac{xt}{2\pi}\right) \cos(rt) dt$$

where

$$G_2(t) = \int_0^{\infty} f(y) \chi_\nu(yt) dy;$$

also by hypothesis

$$\begin{aligned} I_1 &= \int_0^\infty F(y) \psi_\nu(xy) dy \\ &= \frac{1}{x} f(0) + F(x) - \frac{\phi(1)}{x} \\ &= \frac{2}{x} \sum_{r=1}^\infty \int_0^x f(t) \cos \left(\frac{2\pi r t}{x} \right) dt \end{aligned}$$

{by Poisson's theorem [4, p. 60 (2·8·1)] }

$$= \frac{1}{\pi} \sum_{r=1}^\infty \int_0^\infty f \left(\frac{x t}{2\pi} \right) \cos (r t) dt.$$

Hence equating the two values of I_1 , we get

$$\sum_{r=1}^\infty \int_0^\infty G_2 \left(\frac{x t}{2\pi} \right) \cos (r t) dt = \sum_{r=1}^\infty \int_0^\infty f \left(\frac{x t}{2\pi} \right) \cos (r t) dt$$

that is

$$\sum_{r=1}^\infty \int_0^\infty \left\{ G_2 \left(\frac{x t}{2\pi} \right) - f \left(\frac{x t}{2\pi} \right) \right\} \cos (r t) dt = 0.$$

Hence by (2·6), we obtain

$$G_2 \left(\frac{x t}{2\pi} \right) - f \left(\frac{x t}{2\pi} \right) = 0$$

that is

$$f \left(\frac{x t}{2\pi} \right) = \int_0^\infty f(y) \chi_\nu \left(\frac{x y t}{2\pi} \right) dy,$$

which proves the theorem.

Let us consider the integral (for the theorem 4)

$$\begin{aligned} I_2 &= \int_0^\infty P(y) \phi_\nu(xy) dy \\ &= \int_0^\infty \sum_{r=1}^\infty (-1)^{r+1} f \left(\frac{2r-1}{2} y \right) \phi_\nu(xy) dy \\ &= \sum_{r=1}^\infty (-1)^{r+1} \int_0^\infty f \left(\frac{2r-1}{2} y \right) dy \frac{2}{\pi} \int_0^\infty \chi_\nu \left(\frac{2xyt}{\pi} \right) \sin t dt \\ &= \frac{2}{\pi} \sum_{r=1}^\infty (-1)^{r+1} \frac{1}{(2r-1)} \int_0^\infty \sin t dt \int_0^\infty f(y) \chi_\nu \left(\frac{2xyt}{2r-1\pi} \right) dy \\ &= \frac{2}{\pi} \sum_{r=1}^\infty (-1)^{r+1} \frac{1}{(2r-1)} \int_0^\infty \sin t G_1 \left(\frac{2xt}{2r-1\pi} \right) dt \end{aligned}$$

where

$$G_1(t) = \int_0^x f(y) \chi_\nu(y, t) dy;$$

also we have

$$I_2 = \int_0^\infty P(y) \phi_\nu(x, y) dy = P(x) \quad (\text{by hypothesis})$$

And by Poisson's theorem [4, p. 60 (2.8.1)]

$$\begin{aligned} I_2 &= \sum_{r=1}^{\infty} (-1)^{r+1} \frac{1}{x} \int_0^\infty f(t) \sin \left(\frac{2r-1}{2x} \pi t \right) dt \\ &= \frac{2}{x} \sum_{r=1}^{\infty} (-1)^{r+1} \int_0^\infty f \left(\frac{2xt}{\pi} \right) \sin (2r-1)t dt. \end{aligned}$$

Hence, on equating the values of I_2 , we get

$$\begin{aligned} \frac{2}{\pi} \sum_{r=1}^{\infty} (-1)^{r+1} \int_0^\infty G_1 \left(\frac{2xt}{\pi} \right) \sin (2r-1)t dt \\ = \frac{1}{\pi} \sum_{r=1}^{\infty} (-1)^{r+1} \int_0^x f \left(\frac{2xt}{\pi} \right) \sin (2r-1)t dt, \end{aligned}$$

that is

$$\sum_{r=1}^{\infty} (-1)^{r+1} \int_0^\infty \left\{ G_1 \left(\frac{2xt}{\pi} \right) - f \left(\frac{2xt}{\pi} \right) \right\} \sin (2r-1)t dt = 0.$$

Hence by (2.7), we have

$$G_1 \left(\frac{2xt}{\pi} \right) - f \left(\frac{2xt}{\pi} \right) = 0$$

Thus

$$f \left(\frac{2xt}{\pi} \right) = \int_0^\infty f(y) \chi_\nu \left(\frac{2xyt}{\pi} \right) dy,$$

which shows that $f(x)$ is $R_\nu(k, m)$.

The various changes in the order of integration and summation are easily justifiable.

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Interior value Problem of Heat Conduction for a Finite Circular Cylinder

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Abstract

An interior value problem of transient heat conduction in a finite circular cylinder, with the given temperature distribution on any interior plane normal to the axis of the cylinder, being a function of both time and position, has been solved with the help of finite Hankel transform and Laplace transform

Introduction

Most of the problems in the theory of heat conduction require the determination of conditions at interior points when boundary conditions, such as temperature or heat flux, are prescribed at the outside surface. Such problems have been termed 'direct' problems. Correspondingly in the interior value problem or inverse problem of transient heat conduction it is required to determine the temperature or heat flux at the surface when the temperature or heat flux at an interior location is prescribed. Such problems arise in quenching studies [12, 13], in the measurement of aero-dynamic heating, and in indirect calorimetry devices for laboratory use [11].

For the direct problem the well known methods [2] may be applied in a straight forward manner. For the interior value problem or inverse problem, however, special methods are employed. Stolz [14] has tackled the inverse problem with the help of integral equations and numerical methods. Mirsepasi [7] used graphical methods to solve inverse problems. Masket and Vastano [6] solved these problems with the help of Laplace transform and the method of separation of variables and termed them as 'interior value problems'. Burggraf [1] and Sparrow *et al* [11] have tackled inverse problems in cases where the temperature at interior location is a function of time only. Sabherwal [9] has investigated the temperature distribution on the curved surface of a finite circular cylinder, when the temperature distribution on the interior surface of the cylinder is given and employed the technique of integral transforms.

The authors have only investigated the temperature distribution on the curved surface of the finite or infinite cylinder by different techniques, but it appears no attempt has been made so far to determine the temperature distribution on one of the plane ends of the finite circular cylinder, when the temperature distribution is given on any interior plane normal to the axis of the cylinder and the other plane end of the cylinder. The solution of this type of interior value problem is useful in finding the temperature that should be maintained at one of the ends, the temperature at the other end being known, so as to have a required temperature at one of the interior planes of the cylinder at a particular instant.

The study of literature in connection with the heat engines of various kinds clearly indicates that the cylindrical solids have an important role to play and

therefore a study of the temperature variation of these cylindrical solids which are used in the working of compound engines ; [5, p. 220], air compressor [5, p. 104], ordinary steam engine [5, p. 223] and internal combustion engine [5, p. 379], will be of great use.

During a critical study of [4] regarding the temperature variations in the solid cylindrical fuel elements [4, pp. 200-201] and cylindrical reactor core [4, p. 214, Ex. 9-2], it is observed that the study has been limited to steady state condition when the temperature distribution is a function of radius only. We feel that it will be useful to investigate the temperature distribution in the transient case, when the effect of the difference of temperature at the two ends also affects the situation.

A problem regarding the diffusion of liquid in porous cylinder with its ends coated has been already dealt with [8, p. 317]. The present problem can be extended for solving the diffusion problem in a porous cylinder if its curved surface be coated, so that the liquid diffuses along the axis of the cylinder, by interpreting the temperature function $u(r, z, t)$ as the concentration of the liquid $c(r, z, t)$ and k as the diffusivity constant of proportionality.

In this communication, an interior value problem of transient heat conduction in a finite circular cylinder, with the given temperature distribution on any interior plane normal to the axis of the cylinder, being a function of both time and position, has been solved with the help of finite Hankel transform and Laplace transform.

We feel that this problem is likely to prove more useful than the problems tackled by earlier authors.

Statement of the problem :

Consider the radial and axial heat flow in a finite circular cylinder bounded by the surfaces $z = 0$, $z = h$, and $r = a$, and initially at a temperature zero.

Mathematically the problem is formulated as below :

$$(1) \quad \frac{\partial u}{\partial t} = k \left(\frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} + \frac{\partial^2 u}{\partial z^2} \right) \quad 0 < r < a, \quad 0 < z < h, \quad t > 0,$$

where k is the diffusivity, subject to the conditions

$$(2) \quad \begin{aligned} u(r, 0, t) &= s(r, t), \text{ unknown ;} \\ u(r, z, 0) &= u(r, h, t) = u(a, z, t) = 0 ; \\ u(r, \xi, t) &\text{, known, } 0 < \xi < h \end{aligned}$$

Solution of the Problem :

We apply the finite Hankel transform [10, p. 83] with respect to r , defined as,

$$U(\alpha_n, z, t) = \int_0^a r u(r, z, t) J_0(r\alpha_n) dr$$

where α_n is a root of the transcendental equation

$$J_0(a\alpha_n) = 0,$$

to equations (1) and (2), and obtain

$$(3) \quad \frac{\partial U}{\partial t} = k \left(\frac{\partial^2 U}{\partial z^2} - \alpha_n^2 U \right)$$

with

$$(4) \quad \begin{aligned} U(\alpha_n, 0, t) &= S(\alpha_n, t), \text{ unknown;} \\ U(\alpha_n, z, 0) &= U(\alpha_n, h, t) = 0; \\ U(\alpha_n, \xi, t), &\quad \text{"known"} \end{aligned}$$

Further, applying the Laplace transform with respect to t given by

$$\bar{U}(\alpha_n, z, p) = \int_0^\infty U(\alpha_n, z, t) \exp(-pt) dt$$

to equations (3) and (4), we obtain

$$(5) \quad \frac{d^2 \bar{U}}{dz^2} - (\alpha_n^2 + p/k) \bar{U} = 0$$

with

$$(6) \quad \begin{aligned} \bar{U}(\alpha_n, 0, p) &= \bar{S}(\alpha_n, p), \text{ unknown;} \\ \bar{U}(\alpha_n, h, p) &= 0; \\ \bar{U}(\alpha_n, \xi, p), &\quad \text{"known"} \end{aligned}$$

The solution of (5) with condition (6) will be

$$(7) \quad \bar{U}(\alpha_n, z, p) = \bar{S}(\alpha_n, p) \frac{\text{Sinh}[(h-z)(\alpha_n^2 + p/k)^{\frac{1}{2}}]}{\text{Sinh}[h(\alpha_n^2 + p/k)^{\frac{1}{2}}]}$$

The inverse Laplace transform of

$$\begin{aligned} & \frac{\text{Sinh}[(h-z)(\alpha_n^2 + p/k)^{\frac{1}{2}}]}{\text{Sinh}[h(\alpha_n^2 + p/k)^{\frac{1}{2}}]} \\ &= \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{\text{Sinh}[(h-z)(\alpha_n^2 + p/k)^{\frac{1}{2}}]}{\text{Sinh}[h(\alpha_n^2 + p/k)^{\frac{1}{2}}]} \exp(pt) dp. \end{aligned}$$

The integrand has simple poles at $p = -k(\alpha_n^2 h^2 + m^2 \pi^2)/h$, $m = 0, 1, 2, \dots, \infty$, which give rise to the residues

$$\frac{2\pi km}{h^2} \sin\left(\frac{m\pi z}{h}\right) \exp\left[-\frac{(\alpha_n^2 h^2 + m^2 \pi^2)}{h^2} kt\right]$$

Combining these with the inverse of $\bar{S}(\alpha_n, p)$, namely $S(\alpha_n, t)$ by the convolution theorem [3, p. 37] and summing, we have

$$(8) \quad \begin{aligned} U(\alpha_n, z, t) &= \frac{2\pi k}{h^2} \sum_{m=1}^{\infty} m \sin\left(\frac{m\pi z}{h}\right) \\ &\times \int_0^t S(\alpha_n, T) \exp\left[-\frac{(\alpha_n^2 h^2 + m^2 \pi^2) k (t-T)}{h^2}\right] dT. \end{aligned}$$

From (7) with $z = \xi$, we get

$$(9) \quad \bar{S}(\alpha_n, p) = \bar{U}(\alpha_n, \xi, p) \frac{\text{Sinh}[h(\alpha_n^2 + p/k)^{\frac{1}{2}}]}{\text{Sinh}[(h-\xi)(\alpha_n^2 + p/k)^{\frac{1}{2}}]}$$

Now obtaining inverse Laplace transform of (9), we get

$$(10) \quad S(\alpha_n, t) = \frac{2\pi k}{(h-\xi)^2} \sum_{m=1}^{\infty} (-1)^{m+1} m \sin \left(\frac{m\pi h}{h-\xi} \right) \\ \times \int_0^t U(\alpha_n, \xi, T) \exp \left[- \frac{\{\alpha_n^2 (h-\xi)^2 + m^2 \pi^2\} k (t-T)}{(h-\xi)^2} \right] dT.$$

Further applying inverse finite Hankel transform [10, p. 83] to equation (9), we obtain the solution of the interior value problem

$$(11) \quad s(r, t) = \frac{4\pi k}{a^2 (h-\xi)^2} \sum_n \frac{J_0(r\alpha_n)}{[J_1(a\alpha_n)]^2} \sum_{m=1}^{\infty} (-1)^{m+1} m \sin \left(\frac{m\pi h}{h-\xi} \right) \\ \times \int_0^t U(\alpha_n, \xi, T) \exp \left[- \frac{\{\alpha_n^2 (h-\xi)^2 + m^2 \pi^2\} k (t-T)}{(h-\xi)^2} \right] dT$$

where the summation \sum_n is over the positive roots of the equation $J_0(a\alpha_n) = 0$.

The corresponding solution of the boundary value problem will be obtained by applying the inverse finite Hankel transform [10, p. 83] to (8)

$$(12) \quad u(r, z, t) = \frac{4\pi k}{a^2 h^2} \sum_n \frac{J_0(r\alpha_n)}{[J_1(a\alpha_n)]^2} \sum_{m=1}^{\infty} m \sin \left(\frac{m\pi z}{h} \right) \\ \times \int_0^t S(\alpha_n, T) \exp \left[- \frac{(\alpha_n^2 h^2 + m^2 \pi^2) k (t-T)}{h^2} \right] dT$$

where the summation \sum_n is over the positive roots of the equation $J_0(a\alpha_n) = 0$.

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Chemical Examination of the Root of *Butea monosperma* Isolation and study of ceryl alcohol, β -sitosterol and some higher fatty acids

By

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Abstract

The petroleum ether extract of the root of *Butea monosperma* when kept overnight, deposited a residue which was separated by filtration. The deposit was found to be ceryl alcohol. On distilling off the solvent from the filtrate, a fat was obtained which has been found to contain lignoceric, palmitic, oleic and linoleic acids. The unsaponifiable matter has been found to be β -sitosterol.

Introduction

Butea monosperma^{1,2}, (Hindi-Palas, N. O. Leguminosae) is commonly found throughout the greater parts of India and Burma upto 3000 feet and higher in the outer Himalayas. The root cures night blindness and other defects of sight, and is useful in elephantiasis. It is also reported to make a woman sterile temporarily.

Experimental

About 10 kg of dried and powdered root were extracted with petroleum ether (40–60°C) in a soxhlet extractor. The petroleum ether extract was kept overnight when a white deposit was obtained. The deposit was separated by filtration.

Study of the deposit

The deposit on repeated crystallisation from hot benzene yielded a pure compound melting at 79°C. This compound neither contained phosphorus, halogens, nitrogen or sulphur nor it gave the reactions of acids, aldehydes, ketones, lactones or sterols.

Found
C = 81.32%, H = 13.6%
Molecular Weight = 308
(Semi-micro – Rast)

Calculated for $C_{26}H_{54}O$
C = 81.67%, H = 14.13%
Molecular Weight = 312

It furnished a monoacetate m. p. 67°C and was identified as ceryl alcohol by mixed melting point and infrared spectrum. Peaks in the I. R. spectrum were found at 3498, 2885, 2300, 1730, 1470 and 730 cm^{-1} .

Isolation and study of the fat

After the separation of the deposit, the petroleum ether extract was concentrated, when a semi-solid fat was obtained. A known amount of the fat was saponified and the mixed fatty acids were recovered by the usual procedure. The mixed fatty acids [acid value 8.4, saponification value 184.7, and iodine value 85.6] (Hanus method) were segregated into solid and liquid fractions by Twitche'll's lead salt alcohol process³ modified by Hilditch and co-workers⁴.

The solid and liquid fatty acids were further fractionated by methyl ester distillation method and the presence of individual acids in each fraction was found by determining saponification and iodine values.

A qualitative study of each fraction was done by paper chromatography. For the study of solid acids Whatman No. 1 filter paper impregnated with 10% solution of liquid paraffin in benzene and acetic acid water (7:1) as solvent were used. The chromatograms after development were heated at 80–100°C and were immersed in 1000 ml of water containing 20 ml of saturated solution of copper-acetate. The paper was washed with water containing 0.01% acetic acid and was then dipped into a solution of 1.5% aqueous potassium ferrocyanide^{5,6,7,8}.

A qualitative study of the liquid acids was made with Whatman No. 1 filter paper impregnated with 2% olive oil (Kobrlc 1954) as chromatogram and 75% ethanol as solvent. The developed chromatograms were then treated with saturated solution of copper acetate followed by 1.5% aqueous solution of potassium ferrocyanide^{5,6,7,8}.

As a result of these examinations, the component fatty acids of the fat from the root of *Butea monosperma* were found to be lignoceric, palmitic, oleic and linoleic acids, the fact being in good agreement with the component fatty acids of the oil from the seed of *Butea monosperma*, reported by earlier workers⁹.

Examination of unsaponifiable matter.

After the saponification of the fat, the unsaponifiable matter was removed by shaking the aqueous solution of soap with ether. The solvent was distilled off and the product obtained was then chromatographed over neutral alumina. Elutions with benzene : petroleum ether (2 : 9) mixture furnished a crystalline product which was recrystallised from methanol when fine needles, melting at 137°C, were obtained. This compound underwent Liebermann–Burchard reaction for sterols indicating it to be a sterol.

Found	$C_{29}H_{50}O$ requires
C = 81.54%, H = 11.32%	C = 81.05%, H = 12.07%
$[\alpha]_D^{30} = -35.2$ (CHCl ₃)	$[\alpha]_D^{30} = -36.6$

On acetylation with acetic anhydride and pyridine, it gave a monoacetate melting at 127–128°C.

Found	Calculated for $C_{31}H_{52}O_2$ (mono acetate)
C = 81.62%, H = 11.38%	C = 81.57%, H = 11.4%

The peaks in the I. R. spectrum were found at 3500 cm.⁻¹, 1640 cm.⁻¹, 1470 cm.⁻¹ and 1445 cm.⁻¹, which showed its identity with β -sitosterol.

The melting point of the compound was not depressed when mixed with an authentic sample of β -sitosterol. Thus, the compound was confirmed to be β -sitosterol.

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Congruences for $\sigma(n)$

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1. Introduction

K. G. Ramanathan⁵ had shown that $\sigma(n)$ defined as the sum of the divisors of an integer n , satisfies the congruence properties

$$(1.1) \quad \sigma(jn - 1) \equiv 0 \pmod{j} \text{ for } j = 3, 4, 6, 8, 12 \text{ or } 24.$$

It was shown by H. Gupta³ that these are the only congruences of this type. New proofs for these results were given by M. V. Subba Rao⁶. In this note we propose to give a new and simple proof for the congruences (1.1).

2. In proving the above congruences we shall use the following theorem due to Bambah, Chowla, Gupta and Lahiri¹, that if j be a divisor of 24 and $(n, j) = 1$, then

$$(2.1) \quad \tau(n) \equiv \sigma(n) \pmod{j}$$

and Ramanujan's result⁴ that

$$(2.2) \quad \tau(n) = \frac{24}{1-n} \sum_{\gamma=1}^{\infty} \tau(n-\gamma) \sigma(\gamma)$$

where $\tau(n)$ is defined by

$$(2.3) \quad x[(1-x)(1-x^2)(1-x^3)\dots]^{24} = \sum_{n=1}^{\infty} \tau(n)x^n.$$

Since $\tau(n)$ are integers⁴, from (2.2), it follows that

$$(2.4) \quad \tau(n) \equiv 0 \pmod{24/d}, \quad d = (24, n-1).$$

Hence from (2.1) and (2.4), it follows that

$$(2.5) \quad \sigma(n) \equiv 0 \pmod{t}$$

t being the G. C. D. of $24/d$ and j and $(n, j) = 1$. Now consider $n = jm - 1$ then since $(jm - 1, j) = 1$, (2.5) yields

$$(2.6) \quad \sigma(jm - 1) \equiv 0 \pmod{t}$$

where t is the G. C. D. of $24/d$ and j , and d is the greatest of the integers 1, 2, 3, 4, 6, 8, 12 or 24 which divides $jm - 2$.

Considering $j = 3, 4, 6, 12$, from (2.6) we get

$$(2.7) \quad \sigma(jm - 1) \equiv 0 \pmod{j} \text{ for } j = 3, 4, 6, 12$$

and

$$(2.8) \quad \sigma(jm-1) \equiv 0 \pmod{j/2} \text{ for } j = 8 \text{ and } 24.$$

To complete the proof of (1.1), we have only to show that the modulus in (2.8) is j instead of $j/2$.

In (2.2), put $n = jm - 1$, we get

$$(2.9) \quad \tau(jm-1) = -\frac{24}{jm-2} \sum_{\gamma=1}^{jm-2} \tau(jm-1-\gamma) \sigma(\gamma).$$

Now since it is well known that $\tau(n)$ is odd only when n is an odd square¹, to know the parity of

$$\sum_{\gamma=1}^n \tau(n-\gamma) \sigma(\gamma), \text{ we have to consider the terms of the form}$$

$$\tau(4k^2 + 4k + 1) \sigma(jm - 4k^2 - 4k - 2).$$

When $j = 8$ or 24 , $\sigma(jm - 4k^2 - 4k - 2)$ is only of the form $\sigma(8R + 6)$, which is even, since $\sigma(n)$ is odd only when n is a square or double of a square [2, pp. 284]. Hence

$$\sum_{\gamma=1}^{jm-2} \tau(jm-1-\gamma) \sigma(\gamma) \equiv 0 \pmod{2} \text{ for } j = 8 \text{ and } 24.$$

Therefore in view of (2.1),

$$(2.10) \quad \sigma(jm-1) \equiv 0 \pmod{j} \text{ for } j = 8 \text{ or } 24 \text{ also.}$$

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Some Infinite Integrals Involving Generalized Hypergeometric functions ψ_2 and F_c

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Abstract

In this paper a theorem on Laplace transform has been established. With the help of this theorem a number of infinite integrals involving the Lauricella's hypergeometric function F_c and the generalized confluent hypergeometric function ψ_2 have been evaluated. The argument of these functions contain $(a + bt + ct^2)/t$ where 't' is the variable of integration. A number of very interesting particular cases of these results involving Appell's function F_4 , hypergeometric functions ${}_4F_3$, ${}_3F_3$, ${}_2F_1$, ${}_1F_1$ and modified Bessel function of first kind I_ν have been derived.

1. Introduction

In this paper a theorem on Laplace transform has been proved. With the help of this theorem a number of infinite integrals involving the Lauricella's hypergeometric function of n -variables F_c [1, p. 114] and the generalized confluent hypergeometric function ψ_2 [1, p. 134], have been evaluated. The argument of these function contain $(a + bt + ct^2)/t$ where 't' is the variable of integration. A number of very interesting particular cases of these results involving Appell's function F_4 , hypergeometric functions ${}_4F_3$, ${}_3F_3$, ${}_2F_1$, ${}_1F_1$ and modified Bessel function of the first kind I_ν have been derived.

In this paper we shall denote the Laplace transform

as

$$L\{f(t); p\} = p \int_0^\infty e^{-pt} f(t) dt.$$

2. Theorem on Laplace transform

If

$$L\{f(t); p\} = h(p)$$

and

$$L\{t^{-\frac{1}{2}} f(t); p\} = g(p)$$

then

$$(2.1) \quad \int_0^\infty t^{\frac{1}{2}} (a + bt + ct^2)^{-1} h\left(\frac{a + bt + ct^2}{t}\right) dt = \sqrt{\frac{\pi}{c}} (b + 2\sqrt{ac})^{-1} g(b + 2\sqrt{ac})$$

The above theorem is valid for the set of conditions given below,

(A) $R(a) \geq 0$, $R(c) > 0$.

(B) $R(\xi + \frac{1}{2}) > 0$, where $f(t) = O(t^\xi)$ for small t .

(C) (i) If $r < 1$ then $R(b + 2\sqrt{ac}) > 0$

(ii) If $r = 1$; then $R(\beta) < 0$ when $R(b + 2\sqrt{ac}) > R(\beta)$
and $R(n + \frac{1}{2}) < 0$ when $R(b + 2\sqrt{ac}) = R(\beta)$

(iii) If $r > 1$ then $R(\beta) < 0$

where $f(t) = O(t^n e^{\beta t^r})$ for large 't'.

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Proof : We have

$$\begin{aligned}
 & \int_0^\infty t^{\frac{1}{2}}(a+bt+ct^2)^{-1} h\left(\frac{a+bt+ct^2}{t}\right) dt \\
 &= \int_0^\infty t^{\frac{1}{2}}(a+bt+ct^2)^{-1} \left\{ \frac{a+bt+ct^2}{t} \int_0^\infty \exp. \left\{ -x \frac{a+bt+ct^2}{t} \right\} f(x) dx \right\} dt \\
 &= \sqrt{\frac{\pi}{c}} \int_0^\infty \exp. (-bx - 2\sqrt{ac}x) x^{-\frac{1}{2}} f(x) dx \\
 &= \sqrt{\frac{\pi}{c}} (b + 2\sqrt{ac})^{-1} g(b + 2\sqrt{ac}),
 \end{aligned}$$

on changing the order of integration and evaluating the 't' integral by means of the following result [5, p. 146].

$$(2.2) \quad \int_0^\infty t^{-\frac{1}{2}} \exp. \left(-\frac{a+ct^2}{t} \right) dt = \sqrt{\frac{\pi}{c}} \exp. (-2\sqrt{ac}),$$

for $R(a) \geq 0$ and $R(c) > 0$.

The change of order of integration involved here is justified by the application of de la Vallée Poussins theorem, [2, p. 504], for the conditions given with the theorem, when

(i) the 't' integral is absolutely convergent. This is so if,

$$R(a) \geq 0, R(c) > 0,$$

(ii) the 'x' integral is absolutely convergent. This is so if,

$R(1+\xi) > 0$ where $f(x) = O(x^\xi)$ for small 'x', and if,

(A) $r < 1$ then $R(a) > 0$,

(B) $r = 1$ then $R(a) \geq 0$ and $R(\beta) < 0$

(C) $r > 1$ then $R(\beta) < 0$

where $f(x) = O(x^\eta e^{\beta x^r})$ for large 'x',

(iii) either of the resulting integral is absolutely convergent,

for r. h. s. to exist, $R(\frac{1}{2} + \xi) > 0$, and if

(A) $r < 1$ then $R(b + 2\sqrt{ac}) > 0$

(B) $r = 1$ then $R(b + 2\sqrt{ac} - \beta) > 0$ [and if $R(b + 2\sqrt{ac} - \beta) = 0$
then $R(\eta + \frac{1}{2}) < 0$]

(C) $r > 1$ then $R(\beta) < 0$.

The theorem can also be deduced from [9, p. 154] on taking $\nu = \frac{1}{2}$ after little adjustments.

3. Applications : In this section we illustrate the theorem with some suitable examples. A number of very interesting particular cases are also given.

Example 1

If we start with,

$$f(t) = t^{\nu-1} \prod_{i=1}^n J_2 \mu_i (2 \alpha_i t^{\frac{1}{2}}),$$

then [5, p. 187]

$$h(p) = \frac{\Gamma(\nu+M)}{\Gamma(2\mu_1+1), \dots, \Gamma(2\mu_n+1)} \frac{p^{1-\nu-M} \alpha_1^{\mu_1} \dots \alpha_n^{\mu_n}}{\Gamma(2\mu_1+1), \dots, \Gamma(2\mu_n+1)} \psi_2 \left(\nu+M; 2\mu_1+1, \dots, 2\mu_n+1; -\frac{\alpha_1}{p}, \dots, -\frac{\alpha_n}{p} \right),$$

where $M = \mu_1 + \dots + \mu_n$, $R(p) > 0$ and $R(\nu + M) > 0$.

Similarly the expression for $g(p)$ can be obtained, and hence using (2.1) we get,

$$(3.1) \quad \begin{cases} \int_0^\infty t^{\nu+M-\frac{1}{2}} (a+bt+ct^2)^{-\nu-M} \psi_2 \left(\nu+M; 2\mu_1+1, \dots, 2\mu_n+1; \right. \\ \quad \left. \frac{-\alpha_1 t}{a+bt+ct^2}, \dots, \frac{\alpha_n t}{a+bt+ct^2} \right) dt \\ \sqrt{\frac{\pi}{c}} (b+2\sqrt{ac})^{\frac{1}{2}-\nu-M} \Gamma(\nu+M-\frac{1}{2}) \{\Gamma(\nu+M)\}^{-1} \psi_2 \left(\nu+M-\frac{1}{2}; \right. \\ \quad \left. 2\mu_1+1, \dots, 2\mu_n+1; -\frac{\alpha_1}{b+2\sqrt{ac}}, \dots, -\frac{\alpha_n}{b+2\sqrt{ac}} \right), \\ \text{for } R(a) \geq 0, R(c) > 0, R(b+2\sqrt{ac}) > 0 \text{ and } R(\nu+M-\frac{1}{2}) > 0. \end{cases}$$

Particular cases

If we put $\alpha_1 = \alpha_2$ and $\alpha_3 = \dots = \alpha_n \rightarrow 0$ then [4, p. 124] (3.1) reduces to the following form,

$$(3.2) \quad \begin{cases} \int_0^\infty t^{\nu+\mu_1+\mu_2-\frac{1}{2}} (a+bt+ct^2)^{-\nu-\mu_1-\mu_2} {}_3F_3 \left(\nu+\mu_1+\mu_2, \mu_1+\mu_2+1, \mu_1+\mu_2+\frac{1}{2}; \right. \\ \quad \left. 2\mu_1+1, 2\mu_2+1, 2\mu_1+2\mu_2+1; \frac{-4\alpha_1 t}{a+bt+ct^2} \right) dt \\ = \sqrt{\frac{\pi}{c}} (b+2\sqrt{ac})^{\frac{1}{2}-\nu-\mu_1-\mu_2} \Gamma(\nu-\frac{1}{2}+\mu_1+\mu_2) \{\Gamma(\nu+\mu_1+\mu_2)\}^{-1} \times \\ {}_3F_3 \left(\nu-\frac{1}{2}+\mu_1+\mu_2, \mu_1+\mu_2+1, \mu_1+\mu_2+\frac{1}{2}; -\frac{4\alpha_1}{b+2\sqrt{ac}} \right), \end{cases}$$

for $R(a) \geq 0$, $R(c) > 0$, $R(b+2\sqrt{ac}) > 0$ and $R(\nu+\mu_1+\mu_2-\frac{1}{2}) > 0$.

If $\alpha_2 = \dots = \alpha_n \rightarrow 0$ then (3.1) reduces to,

$$(3.3) \quad \begin{cases} \int_0^\infty t^{\nu+\mu_1-\frac{1}{2}} (a+bt+ct^2)^{-\nu-\mu_1} {}_1F_1 \left(\nu+\mu_1; 2\mu_1+1; -\frac{\alpha_1 t}{a+bt+ct^2} \right) dt \\ = \sqrt{\frac{\pi}{c}} (b+2\sqrt{ac})^{\frac{1}{2}-\nu-\mu_1} \Gamma(\nu+\mu_1-\frac{1}{2}) \{\Gamma(\nu+\mu_1)\}^{-1} \\ {}_1F_1 \left(\nu+\mu_1-\frac{1}{2}; 2\mu_1+1; \frac{-\alpha_1}{b+2\sqrt{ac}} \right), \end{cases}$$

for $R(a) \geq 0$, $R(c) > 0$, $R(b + 2\sqrt{ac}) > 0$ and $R(\nu + \mu_1 - \frac{1}{2}) > 0$.

If $a \rightarrow 0$ and $b = c = 1$ then (3.3) becomes the particular case of a known result [6, p. 417].

If we put $\nu = \frac{1}{2}$ in (3.3) and use Kummer's second theorem [10, p. 12], then it can be placed in the following form,

$$(3.4) \quad \left\{ \begin{aligned} & \int_0^\infty (a+bt+ct^2)^{-\frac{1}{2}} \exp. \left\{ -\frac{\alpha_1 t}{a+bt+ct^2} \right\} I_{\mu_1} \left(\frac{-\alpha_1 t}{a+bt+ct^2} \right) dt \\ &= \sqrt{\frac{\pi}{c}} (b+2\sqrt{ac})^{\frac{1}{2}-\nu-\mu_1} \alpha_1^{\mu_1} \Gamma(\nu+\mu_1-\frac{1}{2}) \left\{ \Gamma(\nu+\mu_1) \Gamma(1+\mu_1) \right\}^{-1} 2^{-2\mu_1} \\ & \quad {}_1F_1 \left(\mu_1; 2\mu_1+1; -\frac{\alpha_1}{b+2\sqrt{ac}} \right), \end{aligned} \right.$$

for $R(a) \geq 0$, $R(c) > 0$, $R(b+2\sqrt{ac}) > 0$ and $R(\nu+\mu_1-\frac{1}{2}) > 0$.

Example 2

If we start with,

$$f(t) = t^{\sigma-\frac{n}{2}} \prod_{i=1}^n \{J_{\nu_i}(a_i t)\}$$

then [7, p. 162]

$$\begin{aligned} h(p) &= \sqrt{\frac{2}{\pi}} 2^{\sigma-2} \prod_{i=1}^n (a_i)^{\nu_i} p^{\frac{n}{2}-\sum \nu_i-\sigma} \Gamma\left\{\frac{1}{2}(\sigma+\sum \nu_i \pm \frac{1}{2})\right\} \prod_{i=1}^n \{\Gamma(1+\nu_i)\}^{-1} \\ & \times F_c\left\{\frac{1}{2}(\sigma+\sum \nu_i \pm \frac{1}{2}), \frac{1}{2}(\sigma+\sum \nu_i - \frac{1}{2}); 1+\nu_1, \dots, 1+\nu_n; -\frac{\alpha_1^2}{p^2}, \dots, -\frac{\alpha_n^2}{p^2}\right\}, \end{aligned}$$

for $R(\sigma+\sum \nu_i \pm \frac{1}{2}) > 0$, $R(p) > \sum_{i=1}^n |I_m(a_i)|$ and $\sum \nu_i$ stands for $\nu_1 + \dots + \nu_n$.

Similarly the expression for $g(p)$ can be obtained and hence applying (2.1) we get,

$$(3.5) \quad \left\{ \begin{aligned} & \int_0^\infty t^{\sigma+\sum \nu_i-1} (a+bt+ct^2)^{\frac{1}{2}-\sum \nu_i-\sigma} \\ & F_c\left\{\frac{1}{2}(\sigma+\sum \nu_i - \frac{1}{2}), \frac{1}{2}(\sigma+\sum \nu_i + \frac{1}{2}); 1+\nu_1, \dots, 1+\nu_n; \frac{-\alpha_1^2 t^2}{(a+bt+ct^2)^2}, \dots, \right. \\ & \quad \left. \frac{-\alpha_n^2 t^2}{(a+bt+ct^2)^2}\right\} dt \\ &= \sqrt{\frac{\pi}{2c}} (b+2\sqrt{ac})^{1-\sum \nu_i-\sigma} \Gamma\left\{\frac{1}{2}(\sigma+\sum \nu_i)\right\} \Gamma\left\{\frac{1}{2}(\sigma+\sum \nu_i-1)\right\} \\ & \quad [\Gamma\left\{\frac{1}{2}(\sigma+\sum \nu_i \pm \frac{1}{2})\right\}]^{-1} F_c\left\{\frac{1}{2}(\sigma+\sum \nu_i), \frac{1}{2}(\sigma+\sum \nu_i-1); 1+\nu_1, \dots, 1+\nu_n; \right. \\ & \quad \left. \frac{-\alpha_1^2}{(b+2\sqrt{ac})^2}, \dots, \frac{-\alpha_n^2}{(b+2\sqrt{ac})^2}\right\}, \end{aligned} \right.$$

for $R(a) \geq 0$, $R(c) > 0$, $R(b+2\sqrt{ac}) > \sum_{i=1}^n |I_m(a_i)|$ and $R(\sigma+\sum \nu_i-1) > 0$.

Particular cases

When $n = 2$, F_c reduces to Appell's function F_4 and consequently (3.5) reduces to

$$(3.6) \quad \left\{ \begin{aligned} & \int_0^\infty t^{\nu_1 + \nu_2 + \sigma - 1} (a + bt + ct^2)^{\frac{1}{2} - \nu_1 - \nu_2 - \sigma} \\ & F_4 \left(\frac{1}{2}(\sigma + \nu_1 + \nu_2 - \frac{1}{2}), \frac{1}{2}(\sigma + \nu_1 + \nu_2 + \frac{1}{2}); 1 + \nu_1, 1 + \nu_2; \frac{-a_1^2 t^2}{(a + bt + ct^2)^2}, \right. \\ & \quad \left. \frac{-a_2^2 t^2}{(a + bt + ct^2)^2} \right) dt \\ & = \sqrt{\frac{\pi}{2c}} (b + 2\sqrt{ac})^{1 - \nu_1 - \nu_2 - \sigma} \Gamma\{\frac{1}{2}(\sigma + \nu_1 + \nu_2)\} \Gamma\{\frac{1}{2}(\sigma + \nu_1 + \nu_2 - 1)\} \\ & \quad [\Gamma\{\frac{1}{2}(\sigma + \nu_1 + \nu_2 \pm \frac{1}{2})\}]^{-1} F_4 \left(\frac{1}{2}(\sigma + \nu_1 + \nu_2), \frac{1}{2}(\sigma + \nu_1 + \nu_2 - 1); 1 + \nu_1, 1 + \nu_2; \right. \\ & \quad \left. - \frac{a_1^2}{(b + 2\sqrt{ac})^2}, - \frac{a_2^2}{(b + 2\sqrt{ac})^2} \right), \end{aligned} \right.$$

for $R(a) \geq 0$, $R(c) > 0$, $R(b + 2\sqrt{ac}) > |Im(\alpha_1)| + |Im(\alpha_2)|$, and $R(\sigma + \nu_1 + \nu_2 - 1) > 0$.

Further if $a_2 \rightarrow 0$, then (3.6) reduces to the following form :

$$(3.7) \quad \left\{ \begin{aligned} & \int_0^\infty t^{\sigma + \nu_1 - 1} (a + bt + ct^2)^{\frac{1}{2} - \nu_1 - \sigma} {}_2F_1 \left(\frac{1}{2}(\sigma + \nu_1 - \frac{1}{2}), \frac{1}{2}(\sigma + \nu_1 + \frac{1}{2}); \right. \\ & \quad \left. 1 + \nu_1; \frac{a_1^2 t^2}{(a + bt + ct^2)^2} \right) dt \\ & = \sqrt{\frac{\pi}{2c}} (b + 2\sqrt{ac})^{1 - \nu_1 - \sigma} \Gamma\{\frac{1}{2}(\sigma + \nu_1 - 1)\} \Gamma\{\frac{1}{2}(\sigma + \nu_1)\} [\Gamma\{\frac{1}{2}(\sigma + \nu_1 \pm \frac{1}{2})\}]^{-1} \\ & \quad {}_2F_1 \left(\frac{1}{2}(\sigma + \nu_1), \frac{1}{2}(\sigma + \nu_1 - 1); 1 + \nu_1; \frac{-a_1^2}{(b + 2\sqrt{ac})^2} \right), \end{aligned} \right.$$

for $R(a) \geq 0$, $R(c) > 0$, $R(b + 2\sqrt{ac}) > 2|Im(\alpha_1)|$ and $R(\sigma + \nu_1 - 1) > 0$.

(3.7) can be obtained from a known result due to SAXENA [8, p. 663].

BURCHNALL [3, p. 101] has proved the following result :

$$(3.8) \quad F_4(\alpha, \beta; \gamma, \delta; x, x) = {}_4F_3 \left(\alpha, \beta, \frac{1}{2}(\gamma + \delta - 1), \frac{1}{2}(\gamma + \delta); \gamma, \delta, \gamma + \delta - 1; 4x \right)$$

and hence, when $\alpha_1 = \alpha_2$ then (3.6) reduces to the following form :

$$\begin{aligned}
(3.9) \quad & \int_0^\infty t^{\sigma+\nu_1+\nu_2-1} (a+bt+ct^2)^{\frac{1}{2}-\nu_1-\nu_2-\sigma} \\
& {}_1F_3 \left(\begin{matrix} \frac{1}{2}(\sigma+\nu_1+\nu_2-\frac{1}{2}), \frac{1}{2}(\sigma+\nu_1+\nu_2+\frac{1}{2}), \frac{1}{2}(1+\nu_1+\nu_2), \frac{1}{2}(2+\nu_1+\nu_2) \\ 1+\nu_1, 1+\nu_2, 1+\nu_1+\nu_2 \end{matrix} ; \right. \\
& \quad \left. \frac{-4\alpha_1^2 t^2}{(a+bt+ct^2)^2} \right) dt \\
& \sqrt{\frac{\pi}{2c}} (b+2\sqrt{ac})^{1-\nu_1-\nu_2-\sigma} \Gamma\{\frac{1}{2}(\sigma+\nu_1+\nu_2)\} \Gamma\{\frac{1}{2}(\sigma+\nu_1+\nu_2-2)\} \\
& \quad [\Gamma\{\frac{1}{2}(\sigma+\nu_1+\nu_2\pm\frac{1}{2})\}]^{-1} \\
& {}_4F_3 \left(\begin{matrix} \frac{1}{2}(\sigma+\nu_1+\nu_2), \frac{1}{2}(\sigma+\nu_1+\nu_2-1), \frac{1}{2}(1+\nu_1+\nu_2), \frac{1}{2}(2+\nu_1+\nu_2) \\ 1+\nu_1, 1+\nu_2, 1+\nu_1+\nu_2 \end{matrix} ; \right. \\
& \quad \left. \frac{-4\alpha_1^2}{(b+2\sqrt{ac})} \right),
\end{aligned}$$

for $R(a) \geq 0$, $R(c) > 0$, $R(b+2\sqrt{ac}) > 2$ | $I_m(\alpha_1)$ | and $R(\sigma+\nu_1+\nu_2-1) > 0$.

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Complexometric Determination of Rare Earths using Thoron [1-(*o*-Arsonophenylazo)—2 Naphthol-3 : 6 Disulphonate] as an Indicator

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Abstract

1-(*o*-arsonophenylazo)—2-naphthol-3 : 6-disulphonate (Thoron) has been found useful as metal indicator in the complexometric determination, taking erbium as a representative of the rare earth family, using ethylenediaminetetraacetic acid as complexing titrant. Titrations were carried out with concentrations of erbium upto 0.003M within the pH range 5.0 to 6.3, while in more dilute solutions, the end point is not very sharp. Temperature has no effect on the end point. Many of the common ions interfere in the titration; Be (II), Pd (II), Sc (III), Y (III), U (VI), Al (III), oxalate, fluoride and citrate interfere at all concentrations; whereas Cu (II), Ag (I), Au (III), Zn (II), Cd (II), Hg (II), Ba (II), Sr (II), Ca (II), Mg (II), Mn (II), Ru (III), Rh (III), Fe (III), Co (II), Ni (II), Sc (III), Bi (III), Pb (II), V (V), Te (IV), Cr (III), SO_4^{2-} , SO_3^{2-} , NO_2^- , NO_3^- , Cl^- , ClO_3^- , SCN^- , CH_3COO^- , PO_4^{3-} and CO_3^{2-} do not interfere.

Introduction

Dey and coworkers¹ have observed the formation of a red coloured chelate, between rare earths and Thoron [1-(*o*-arsonophenylazo)—2-naphthol 3 : 6-disulphonate] with a λ_{max} at 500 m μ . It was considered to be of interest to utilise this reagent as a metal indicator in the complexometric determination of rare earths by titration against ethylenediaminetetraacetic acid (disodium salt).

The present work was undertaken to work out in detail, conditions for the complexometric determination, taking erbium as a representative of the rare earth family using the reagent as an indicator. The end points were concordant irrespective of whether titrations were performed in hot or cold solutions.

Experimental

Reagent and apparatus: A stock solution (0.01M) of Thoron (B. D. H. Indicator) was prepared in double distilled water.

Erbium chloride solution: A stock solution of erbium chloride (Johnson Matthey & Co.) was prepared in water and standardised by the usual method.

Ethylenediaminetetraacetic acid: 0.1M solution was prepared by dissolving 18.6126 gm. of EDTA (disodium salt; B. D. H.) in 500 ml. and the concentration was checked by titrating against calcium using the procedure described by Goetz *et al*².

Solution of foreign ions: 0.1M solution of different ions were prepared by direct weighing or by standardising the solutions by the usual methods.

Apparatus used: A microburette with a least count of 0.02 ml. was used for measuring the solutions. L and N pH meter was used for pH measurements and operated on 220V/50 cycles A.C. mains.

Observations

Concentration of indicator: The colour change at the end point is from red to yellow. Titrations were carried out with different amounts of indicator in

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order to find out whether the indicator solution has any effect on the titre value. It was observed that although the titre values were not appreciably affected by the concentration of the reagent, yet the best results *i.e.* those giving sharp end points were obtained with 0.2 ml. (4 drops) of 0.02M solution of the reagent per 5 ml. volume of 0.02M erbium chloride.

Effect of dilution : Titrations were carried out with solutions of different concentrations and it was found that the titration of erbium against EDTA or *vice versa* is possible upto 0.003M of both solutions. On more dilution, the end point was not very sharp.

Effect of temperature : The effect of temperature on the end point was found to be negligible and titrations may be performed at all temperatures from 0 to 100°.

Effect of pH : Erbium chloride solution of different pH were used for titration against EDTA and the observations are recorded in the following table

TABLE I
Effect of pH on titration of Erbium with EDTA

pH	4.0	4.5	5.0	5.5	6.3	6.5
0.001M Erbium taken (ml)	5.0	5.0	5.0	5.0	5.0	5.0
0.002M EDTA used (ml)	4.5	4.5	5.0	5.0	5.0	pptn. occurs

It may be seen from the above table that the titrations are thus possible between pH 5.0 and 6.3, but for accurate results, pH 6.0 is recommended after which precipitation starts.

Recommended Procedure : Erbium chloride solution was taken in small flask, pH was adjusted to 6.0 and after adding 0.2 ml of 0.02 M Thoron, it was titrated against a standard EDTA solution run in from the burette with constant stirring till the change of colour from red to yellow was observed. The amount of erbium was determined subsequently.

Interference by Diverse Ions : The effect of a large number of ions were observed on the erbium-EDTA titration using Thoron as an indicator. A known amount of erbium was titrated in the presence of different foreign ions and it was found that beryllium, palladium, scandium, yttrium, lanthanum and other rare earths, uranium, aluminium, oxalate, fluoride and citrate interfere at all concentrations ; while copper, silver, gold, zinc, cadmium, mercury, barium, strontium, calcium, magnesium, manganese, ruthenium, rhodium, iron, cobalt, nickel, selenium, bismuth, lead, vanadium, tellurium, chromium, sulphate, nitrate, chloride, chlorate, thiocyanate, acetate, phosphate and carbonate do not interfere.

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Composition and Stability of Aluminium (III)— 2-(*p*-Sulphophenylazo)-1 : 8-Dihydroxy-Naphthalene- 3 : 6-Disulphonic Acid (SPADNS) Chelate and its Application to the Determination of Aluminium

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Abstract

A detailed study of the composition and stability of aluminium (III)-2-(*p*-sulphophenylazo)-1 : 8-dihydroxy-naphthalene-3 : 6-disulphonic acid (SPADNS) chelate has been made spectrophotometrically. The chelate is violet in colour (λ_{max} at 530 m μ) and stable between pH 2.5 to 5.5. The composition, as determined by different methods, is 1 : 2 (metal : chelating agent). The average value of $\log K$ (K =stability constant) is 9.5 (at 25°; pH 4.5). The system obeys Beer's law over a concentration range of 0.054–1.90 ppm of aluminium. The effective range of photometric determination is 0.32 to 1.60 ppm. of aluminium from Ringbom plot. A tentative suggestion regarding the position of the chelate ring in the complex has also been made. Gallium yields a coloured solution which has practically the same λ_{max} as SPADNS. Indium and thallium do not form complexes.

Introduction

2-(*p*-sulphophenylazo)-1 : 8-dihydroxy-naphthalene-3 : 6-disulphonic acid (SPADNS) was described by Banerjee¹⁻⁶ as a chelometric indicator for the determination of thorium, zirconium and fluoride ions. Datta⁷ used this reagent in complexometric determination of zirconium, while Fleury⁸ studied the lake formation between thorium (IV) and SPADNS and developed photometric methods for determining thorium. Munshi and Dey⁹ recommended it for the colorimetric determination of several rare earths and obtained very high value of molar extinction coefficient ranging from 2.0×10^4 to 5.3×10^4 suggesting it to be very highly sensitive for rare earths. Recently Saxena, Munshi and Dey¹² have found it to be a very sensitive reagent for palladium (II). It has now been observed that SPADNS also forms coloured chelate with aluminium but not with indium and thallium. Gallium yields a coloured solution, which has practically the same λ_{max} as SPADNS. The present communication describes the studies on aluminium-SPADNS chelate.

Experimental

Standard solutions of aluminium sulphate (BDH AnalaR) and SPADNS (BDH indicator), were prepared in double distilled carbon dioxide free water and standardised by the usual methods.

Absorbance measurements were carried out with a Unicam SP 500 spectrophotometer, operated by a Doran Mains Unit connected to 220 V/50 cycles A. C. mains, further stabilised by a constant voltage transformer. 1 cm. thickness of the solution was employed in all the cases by using matched glass cells supplied along with the instrument. All absorbance measurements were noted against a distilled water blank.

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Hydrogen-ion concentrations were measured with Leeds and Northrup direct reading pH indicator operated on the same mains. The electrode system was glass-calomel supplied by the same manufacturers.

All experiments were performed at 25°C. The total volume of the mixtures prepared for the measurements was kept 25 ml. The pH of all the solutions and mixtures was adjusted to 4.5 ± 0.2 by the addition of sodium hydroxide or hydrochloric acid.

Results and Discussion

Properties of the reagent and absorption spectra :

The solutions of the order of 10^{-4} M were employed so that the dye behaved as a true solution. With variation in hydrogen ion concentration SPADNS changes its colour and its region of maximum absorption is found to shift as shown in the table below :

TABLE I
Shift of λ_{max} with change in pH

pH	Region of maximum absorbance in m μ
1.0- 5.0	510
5.0- 9.0	515
9.0-12.5	520

It may be seen from above that there are three regions of maximum absorption and it may be concluded that the reagent exists in three different forms depending upon the pH of the solution.

Nature of the complex :

The method of Vosburgh and Cooper¹³ was followed to determine the nature of the complexes formed in solution. Mixtures containing different ratios of Al : SPADNS were prepared at pH 4.5 ± 0.2 and absorbances were measured. It was found that only one complex having wavelength of maximum absorption at 530 m μ is formed under the conditions of study.

Stoichiometry of the components :

The composition of the chelate was established by (i) the method of continuous variations, (ii) mole ratio method and (iii) the slope ratio method. A large number of observations were taken and some of the typical results are plotted in the figures.

The following table summarises the results on the composition as arrived at from the examination of Figures 1 and 2, when the method of continuous variations was employed using absorbances measurements. In the figures c represents the concentration of aluminium and p , the ratio c'/c , c' being the concentration of SPADNS.

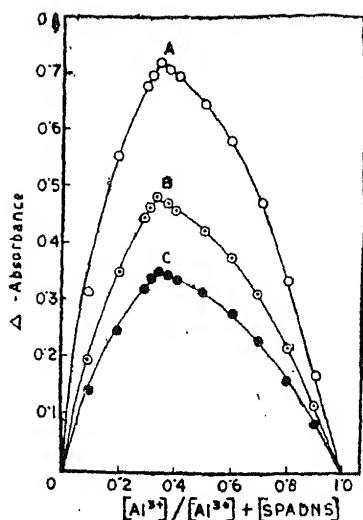


Fig. 1

Determination of the composition by the method of continuous variations using equimolecular solutions at 570 mμ ($p = 1$; pH 4.5).

Curve A : $c = 2.0 \times 10^{-4}$ M ;
Curve B : $c = 1.33 \times 10^{-4}$ M ;
Curve C : $c = 1.0 \times 10^{-4}$ M.

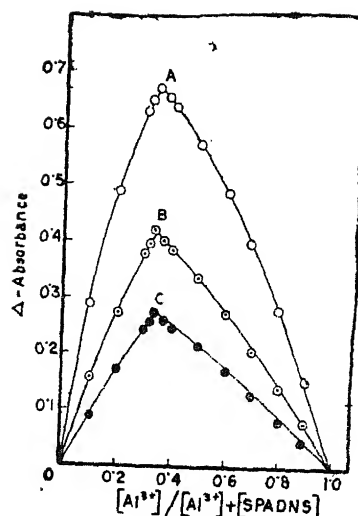


Fig. 2

Determination of the composition by the method of continuous variations using equimolecular solutions at 580 mμ. ($p = 1$). Concentrations and pH same as in Fig. 1.

TABLE 2

Figure	Curve	$c \times 10^4$ (M)	p	Wave-length mμ	Volume of Al (III) at peak (ml)	Composition of the chelate Al (III) : SPADNS
1	A	2.0	1.0	570	8.33	1 : 2
	B	1.33	1.0	570	8.33	1 : 2
	C	1.0	1.0	570	8.33	1 : 2
2	A	2.0	1.0	580	8.33	1 : 2
	B	1.33	1.0	580	8.33	1 : 2
	C	1.0	1.0	580	8.33	1 : 2

It is clear from the above table that the ratio of aluminium to SPADNS in the chelate is 1 : 2 and hence, it may be represented as $\text{Al}(\text{SPADNS})_2$. Results obtained by the other methods also viz., the mole ratio method (Figs. 3 and 4) and the slope ratio method (Figs. 5 and 6) corroborate the same composition of the chelate.

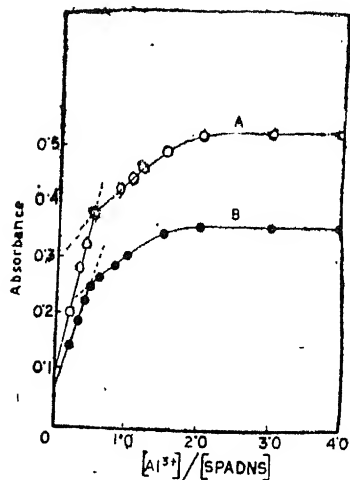


Fig. 3

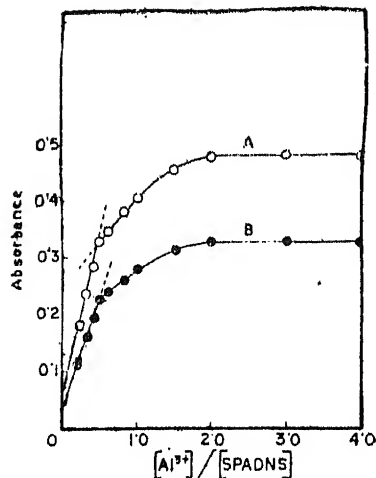


Fig. 4

Determination of the composition from absorbance studies by the mole ratio method at 570 m μ (Fig. 3) and 580 m μ (Fig. 4) respectively, pH 4.5 \pm 0.2. Concentration of SPADNS, A = 6.66×10^{-5} M; B = 5.0×10^{-5} M

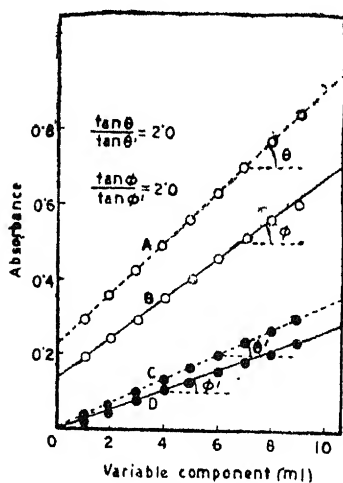


Fig. 5

Determination of the composition by the slope ratio method (pH 4.5). A, C = 570 m μ ; B, D = 580 m μ . 10 ml of 3.34×10^{-4} M excess component + x ml of 1.11×10^{-4} M variable component + (15-x) ml H₂O.

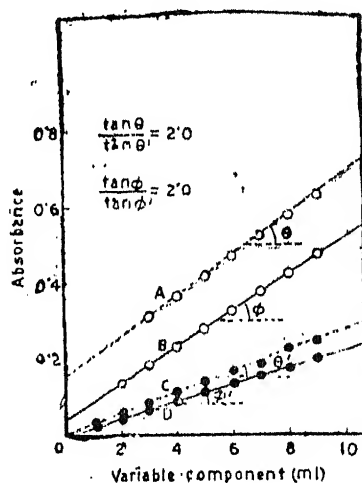


Fig. 6

Determination of the composition by the slope ratio method (pH 4.5). A, C = 570 m μ ; B, D = 580 m μ . 10 ml of 2.50×10^{-4} M excess component + x ml of 0.833×10^{-4} M variable component + (15-x) ml H₂O.

Evaluation of Stability Constant :

The apparent stability constant was calculated from the absorbance data by the method of (a) Dey and coworkers¹⁰⁻¹¹ (b) continuous variations method using non-equimolecular solutions (c) the mole ratio method and (d) by the measurement of molecular extinction coefficient. The temperature was 25° and pH 4.5.

TABLE 3

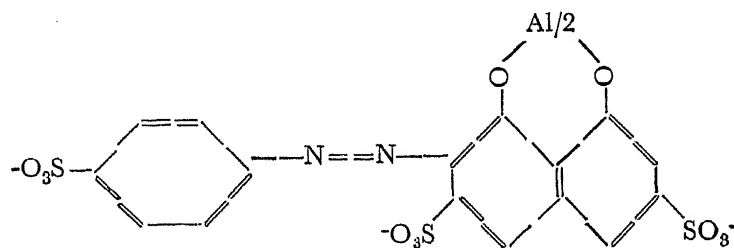
Metal chelate	log <i>K</i>	Method
Al-SPADNS	9.6±0.1	(a)
	9.2±0.1	(b)
	9.2±0.1	(c)
	10.1±0.1	(d)

Analytical applications :

Experiments were performed to test the suitability of the chelate for the colorimetric determination of aluminium. The system was found to adhere to Beer's law in the range of 0.054 to 1.9 ppm. of aluminium in presence of excess reagent absorbance values were consistent over a wide range of temperature between pH 3.5 and 5.5. The effective range of photometric determination determined from Ringbom plot was 0.32 to 1.9 ppm of aluminium. The molar extinction coefficient determined at 570 mμ was 1.59×10^4 .

Suggestions on the structure of the chelate :

Some tentative suggestions may be made about the position of the metal in the chelate. The chelate is anionic in nature as has been noted by electrophoretic experiments and also by the complete adsorption by ion exchange resin Amberlite IR-45 (OH). It is, therefore, likely that the chelation occurs between a pair of phenolic oxygen giving a six membered ring, as follows :



Aluminium (III)-SPADNS chelate

The liberation of hydrogen ions as a result of chelation has qualitatively been noted by observation, a drop of pH when the solution of metal ion and SPADNS is mixed.

Acknowledgment

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On the Dynamics of the Barred Galaxies

By

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Abstract

A homogeneous cylinder, rotating uniformly, is assumed to represent a barred galaxy. The flow of gas, under gravitational force, is investigated. The cartesian coordinates, x and y , have been determined as a function of the parameter ' t '. Numerical solutions confirm the outward flow of gas. The case has been treated when motion commences from a point on the axis of the bar.

Introduction

In a previous paper¹ (subsequently referred to as Paper I) the possibility of the motion of gas, for a barred galaxy, was considered. A homogeneous, uniformly rotating, cylinder was assumed to represent a barred galaxy. The problem was extended for a homogeneous, uniformly rotating, elliptic cylinder as well. The presence of resistance, to the flow of gas, varying as the velocity, was also considered, for both the models.

The problem of the flow of gas appears to deserve more attention. Since in barred spirals non-circular motions are usually present. Burbidge and Burbidge² have found that "some kind of flow in an inward or outward direction, a flow which does not exhibit circular symmetry must occur."

In our previous paper we had assumed following Aarseth^{3,4} and Ôki *et al*⁵ that the y -component of the gravitational force was balanced by the centrifugal force of uniform rotation. Thus we had conditions (3) and (15) in Paper I, which enabled us to obtain the solution of the basic equations. Obviously, these conditions cannot be satisfied every where within the bar. It has been shown, even unfettered from these assumptions, it is possible to obtain the solution of the basic equations.

Basic equations and numerical solutions :

The equations, in rotating coordinates, neglecting non-gravitational forces, will be given by¹

$$\left. \begin{aligned} \frac{d^2x}{dt^2} - 2\Omega \frac{dy}{dt} - \Omega^2 x &= X_c \\ \frac{d^2y}{dt^2} - 2\Omega \frac{dx}{dt} - \Omega^2 y &= Y_c \end{aligned} \right] \quad (1)$$

where Ω is the angular velocity of uniform rotation. The rigid body rotation, for a barred spiral, appears quite a legitimate conclusion as clearly evinced by the rotation curve which is approximately linear along the bar. For outer regions, however, the condition of solid body rotation ceases to be valid. We have⁶

$$X_c = -2\pi G \rho x; Y_c = 0 \quad (2)$$

where the notations have their usual meaning.

$$\left. \begin{aligned} \frac{d^2 x}{dt^2} - 2 \Omega \frac{dy}{dt} + (2 \pi G \rho - \Omega^2) x &= 0 \\ \frac{d^2 y}{dt^2} + 2 \Omega \frac{dx}{dt} - \Omega^2 y &= 0 \end{aligned} \right] \quad (3)$$

The equation in (3) can be written as

$$\left. \begin{aligned} [D^2 + (2 \pi G \rho - \Omega^2)] x - 2 \Omega D y &= 0 \\ [D^2 - \Omega^2] y + 2 \Omega D x &= 0 \end{aligned} \right] \quad (4)$$

From the equations in (4) it follows

$$[D^2 + (2 \pi G \rho - \Omega^2)] [D^2 - \Omega^2] y + 4 \Omega^2 D^2 y = 0 \quad (5)$$

The auxiliary equation is

$$m^4 + 2 (2 \pi G \rho + \Omega^2) m^2 - \Omega^2 (2 \pi G \rho - \Omega^2) = 0 \quad (6)$$

The roots of this biquadratic equation are

$$\begin{aligned} &\pm \{ (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega^2)^{\frac{1}{2}} - (\pi G \rho + \Omega^2)^{\frac{1}{2}} \} \\ \text{and} \quad &\pm i \{ (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega^2)^{\frac{1}{2}} + (\pi G \rho + \Omega^2)^{\frac{1}{2}} \} \end{aligned} \quad (7)$$

The solution of equation (5) is given by

$$y = A e^{\alpha t} + B e^{-\alpha t} + C \cos \beta t + D \sin \beta t \quad (8)$$

where A, B, C and D are arbitrary constants and

$$\left. \begin{aligned} \alpha &= \{ (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega^2)^{\frac{1}{2}} - (\pi G \rho + \Omega^2)^{\frac{1}{2}} \} \\ \beta &= \{ (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega^2)^{\frac{1}{2}} + (\pi G \rho + \Omega^2)^{\frac{1}{2}} \} \end{aligned} \right] \quad (9)$$

From the equations in (4) we have

$$[D^2 - \Omega^2] [D^2 + (2 \pi G \rho - \Omega^2)] x + 4 \Omega^2 D^2 x = 0 \quad (10)$$

The auxiliary equation is found to be equation (6). Hence the solution of equation (10) will differ from the solution of equation (5) only in the value of the arbitrary constants, and thus can be expressed as

$$x = a e^{\alpha t} + b e^{-\alpha t} + c \cos \beta t + d \sin \beta t \quad (11)$$

where a, b, c and d are the new arbitrary constants. In terms of A, B, C and D they can be expressed as

$$\left. \begin{aligned} a &= \frac{2 \Omega \{ (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega^2)^{\frac{1}{2}} - (\pi G \rho + \Omega^2)^{\frac{1}{2}} \}}{\{ (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega^2)^{\frac{1}{2}} + (\pi G \rho - 2 \Omega^2)^{\frac{1}{2}} \}} A \\ b &= \frac{-2 \Omega \{ (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega^2)^{\frac{1}{2}} - (\pi G \rho + \Omega^2)^{\frac{1}{2}} \}}{\{ (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega^2)^{\frac{1}{2}} + (\pi G \rho - 2 \Omega^2)^{\frac{1}{2}} \}} B \\ c &= \frac{2 \Omega \{ + (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega^2)^{\frac{1}{2}} + (\pi G \rho + \Omega^2)^{\frac{1}{2}} \}}{\{ - (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega^2)^{\frac{1}{2}} + (\pi G \rho - 2 \Omega^2)^{\frac{1}{2}} \}} D \\ d &= \frac{-2 \Omega \{ (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega^2)^{\frac{1}{2}} + (\pi G \rho + \Omega^2)^{\frac{1}{2}} \}}{\{ - (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega^2)^{\frac{1}{2}} + (\pi G \rho - 2 \Omega^2)^{\frac{1}{2}} \}} C \end{aligned} \right] \quad (12)$$

With the help of equation (12), equation (11) can be written as

$$x = A \alpha_1 e^{at} - B \alpha_1 e^{-at} + D \beta_1 \cos \beta t - C \beta_1 \sin \beta t \quad (13)$$

where

$$\left. \begin{aligned} \alpha_1 &= \frac{2 \Omega_- \{ (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega_-^2)^{\frac{1}{2}} - (\pi G \rho + \Omega_-^2) \}^{\frac{1}{2}}}{\{ (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega_-^2)^{\frac{1}{2}} + (\pi G \rho - 2 \Omega_-^2) \}} \\ \beta_1 &= \frac{2 \Omega_- \{ (\pi G \rho + \Omega_-^2) + (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega_-^2)^{\frac{1}{2}} \}^{\frac{1}{2}}}{\{ (\pi G \rho - 2 \Omega_-^2) - (\pi^2 G^2 \rho^2 + 4 \pi G \rho \Omega_-^2)^{\frac{1}{2}} \}} \end{aligned} \right] \quad (14)$$

Now we have to evaluate the value of A , B , C and D . Applying the following initial conditions of the problems, $t = 0$; $\frac{dx}{dt} = 0$, $t = 0$, $x = x_0$ and when $t = 0$, $\frac{dy}{dt} = V_c$; $t = 0$, $y = R_1$, we have

$$\left. \begin{aligned} A \alpha \alpha_1 + B \alpha \alpha_1 - C \beta \beta_1 &= 0 \\ A \alpha_1 - B \alpha_1 + D \beta_1 &= x_0 \\ A \alpha - B \alpha + D \beta &= V_c \\ A + B + C &= R_1 \end{aligned} \right] \quad (15)$$

From the above four relations we get the value of A , B , C and D as

$$\left. \begin{aligned} A &= \frac{1}{2} \left[\frac{x_0 \beta - V_c \beta_1}{\beta \alpha_1 - \alpha \beta_1} + \frac{R_1 \beta \beta_1}{\alpha \alpha_1 + \beta \beta_1} \right] \\ B &= \frac{1}{2} \left[\frac{R_1 \beta \beta_1}{\alpha \alpha_1 + \beta \beta_1} - \frac{x_0 \beta - V_c \beta_1}{\beta \alpha_1 - \alpha \beta_1} \right] \\ C &= \frac{R_1 \alpha \alpha_1}{\alpha \alpha_1 + \beta \beta_1} \\ D &= \frac{V_c \alpha_1 - x_0 \alpha}{\beta \alpha_1 - \alpha \beta_1} \end{aligned} \right] \quad (16)$$

The motion of the gas element is to be obtained by equation (8) and equation (13).

Assuming the following model ^{6,7}

$$\left. \begin{aligned} \Omega_- &= 1.43 \times 10^{-15} \text{ radian/sec ; Width of the bar} = 2 \text{ kpc.} \\ R_1 &= 3 \text{ kpc ; } R_2 = 8 \text{ kpc ; Mean density of the bar, } \rho = \\ &4.2 \times 10^{-23} \text{ gm/cm}^3 \end{aligned} \right] \quad (17)$$

We find

$$\left. \begin{aligned} \alpha &= .3706 \times 10^{-7} ; \beta = 1.516 \times 10^{-7} \\ \alpha_1 &= .1982 ; \beta_1 = -1.828 \end{aligned} \right] \quad (18)$$

If motion commences from a point on the axis of the cylinder the numerical value of A , B , C and D will be given by

$$\left. \begin{aligned} A &= 2.0204 ; B = 1.0616 \\ C &= -8.168 \times 10^{-2} ; D = .1040 \end{aligned} \right] \quad (19)$$

also

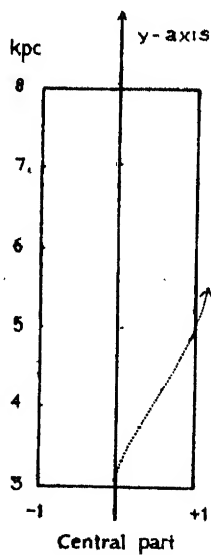
$$\left. \begin{aligned} A a_1 &= .4005 ; & B a_1 &= .2104 \\ D \beta_1 &= -.1901 ; & C \beta_1 &= .1493 \end{aligned} \right] \quad (20)$$

Tables I gives the value of x and y for different values of t .

TABLE 1

t (yrs)	y (kpc)	x (kpc)
0	3.00	.00
1×10^6	3.05	.00
5×10^6	3.33	.07
10×10^6	3.76	.28
15×10^6	4.26	.59
20×10^6	4.84	.91
25×10^6	5.52	1.17

Graph 1 shows the outward motion of gas with increasing time.



It can be seen for $V_c > 0$ the gas will generally move outwards, and may even constitute the leading or trailing spiral arms. The dark lanes of the barred galaxies, which indicate the inward motion of gas, towards the nucleus, can be

easily accounted if $V_c < 0$. The inward motion of gas may be due to the exchange of angular momentum between the bar and the gas streaming outwards.

In another communication it is proposed to discuss motion of gas for other values of κ_0 . The effect of resistance will also be considered, by taking a convenient resistance law.¹ The spheroidal-cylinder model, for the barred galaxy, will also be discussed, since a slightly flattened central nucleus, with cylindrical arms, will be a more realistic choice for the rotating system.

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It is a pleasure to thank Prof. A. C. Banerji, ex-Vice-Chancellor and Emeritus Professor of Mathematics, Allahabad University, for the valuable discussions that I had with him. I am to thank Prof. T. Ôki of Astronomical Institute, Sendai, Japan, for kindly providing me the data on the barred galaxy⁷, and acknowledging the typographical error in the paper⁵. In the end, I thank the Council of Scientific and Industrial Research (India) for the award of the research grant.

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Spectrophotometric Study of Chelate Formation of Hexavalent Uranium with Pyrocatechol Violet

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Abstract

Spectrophotometric study of colour forming reaction between hexavalent uranium and Pyrocatechol Violet (3, 3', 4'-trihydroxyfuchson-2''-sulfonic acid) has been made. The Sandell sensitivity of colour reaction is $0.018 \gamma / \text{cm}^2$. The colour system adheres Beer's law over concentration range 34.3 to 0.8 ppm of uranium. Ringbom optimum range and % relative error per 1% absolute photometric error come out to be 30.5 to 3.8 ppm of uranium and 5.1 respectively. The composition ($\text{UO}_2^{++} : \text{PCV}$) of the chelate formed has been confirmed by the methods of continuous variations and mole ratio. The chelate is stable between pH range 5.5 to 7.0. The values of $\log K$ were found to be of the order of 4.6, the λ_{max} of the greenish blue chelate is $600 \text{ m}\mu$.

Introduction

Microdetermination of uranium (VI) with Pyrocatechol Violet as reagent is possible, when present singly, as it forms greenish violet chelate at pH 6.5. Pyrocatechol violet belongs to the class of sulphonphthalein dyes and was obtained by the condensation of o-sulfobenzoic anhydride with pyrocatechol.¹ It has been extensively used as chelatometric indicator and colorimetric reagent for microdetermination of various metal ions in solution. Recently Malik², and Mushran and coworkers³ have investigated its chelates with tin (IV) and vanadium (IV).

In the present communication the composition, nature, stability constant and analytical possibilities of the U(VI)-Pyrocatechol Violet are reported.

Experimental

Uranyl nitrate solution : Standard solution of uranyl nitrate (A. R., B. D. H.) was prepared by dissolving the salt in double distilled water and standardising by usual methods.

Pyrocatechol Violet solution : Standard reagent solution was prepared by dissolving a weighed quantity (B. D. H.) in double distilled water.

Apparatus : Beckman (DU) spectrophotometer was used for absorbance measurements. For pH measurements, a Leeds and Northrup direct reading pH indicator with glass and calomel electrodes was employed. The instrument was standardised from time to time with a standard buffer supplied with the instrument.

Results

It has been observed that order of addition of reactants had no appreciable effect on the absorbance. The colour formation is instantaneous and the intensity of colour remained constant for about twenty four hours. Measurements were made at 25°C. All the experiments were performed at pH 6.5, keeping volume 25 ml. pH of all the mixtures was separately adjusted to 6.5 by addition of suitable amounts of acid or alkali.

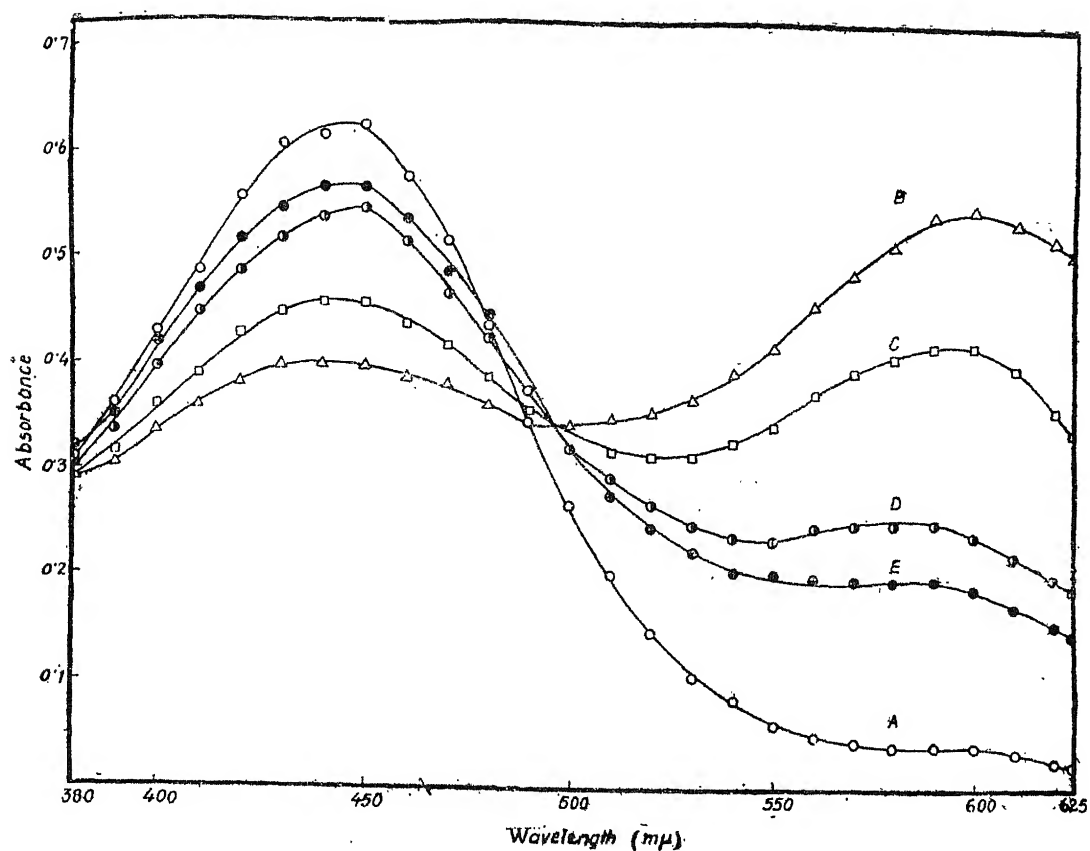


Fig. 1. Absorption spectra of U(VI)-PGV chelate ;
Total volume 25 ml ; pH 6.5 ; Temp. 25°C.

Curve	Final concentration $M \times 10^{-5}$		Ratio $UO_2^{++} : PGV$
	$UO_2(NO_3)_2$	PGV	
A	0.00	4.00	0 : 4.0
B	8.00	4.00	2 : 1.0
C	4.00	4.00	1 : 1.0
D	2.00	4.00	1 : 2.0
E	1.33	4.00	1 : 3.0

Nature of Complexes formed: The method of Vosburgh and Cooper⁴ was employed for determination of the nature of complexes formed in solution. Mixtures containing different proportions of uranyl nitrate and Pyrocatechol Violet were prepared at pH 6.5. Absorbance of each of them was measured at suitable wavelength intervals. The absorbance values corresponding to different wavelengths of different mixtures are plotted against wavelength in Fig. 1. This figure clearly indicates the formation of one complex having wavelength of maximum absorbance as 600 m μ .

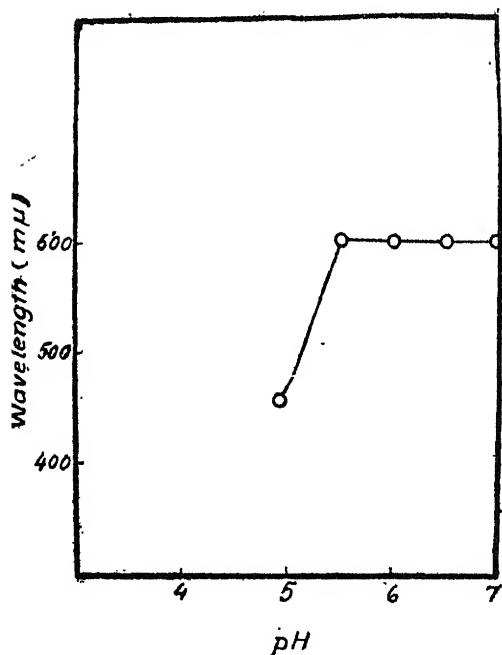


Fig. 2. Variation of λ_{max} of chelate with pH.

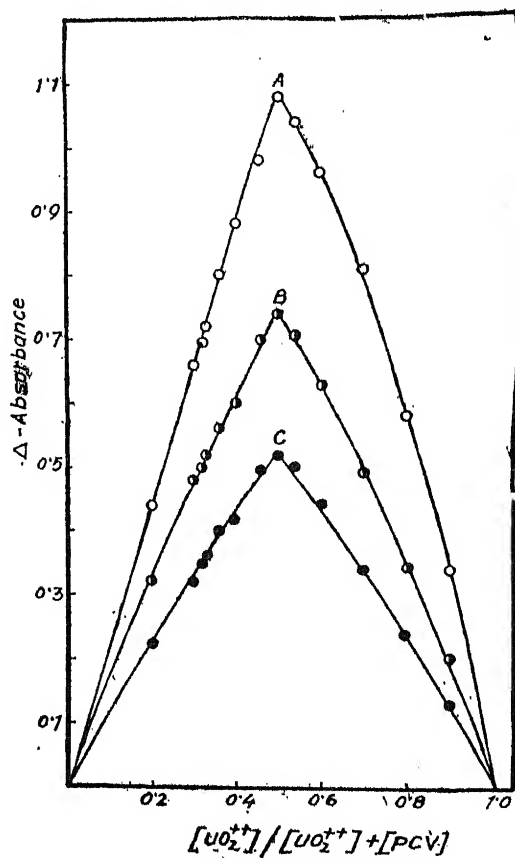


Fig. 3. Determination of chelate composition by method of continuous variation at 600 m μ ; pH 6.5; concentration of $\text{UO}_2(\text{NO}_3)_2$ and PCV, curve A, 2.00×10^{-4} M, curve B, 1.33×10^{-4} M, curve C, 1.00×10^{-4} M.

pH stability range of the chelate: Various mixtures containing uranyl nitrate and reagent in stoichiometric ratio were prepared at different pH values, keeping

total volume 25 ml. Absorbance of each mixture was measured at suitable wavelength intervals. The wavelength of maximum absorbance of different mixtures are plotted against pH in Fig. (2). The pH range over which the λ_{max} of the chelate holds good was taken as the pH stability range of the chelate. The chelate is stable between pH 5.5 to 7.0.

Composition of the chelate: Composition (UO_2^{++} : PCV) was confirmed by method of continuous variation ⁵ (Fig. 3) and mole ratio ⁶ (Fig. 4).

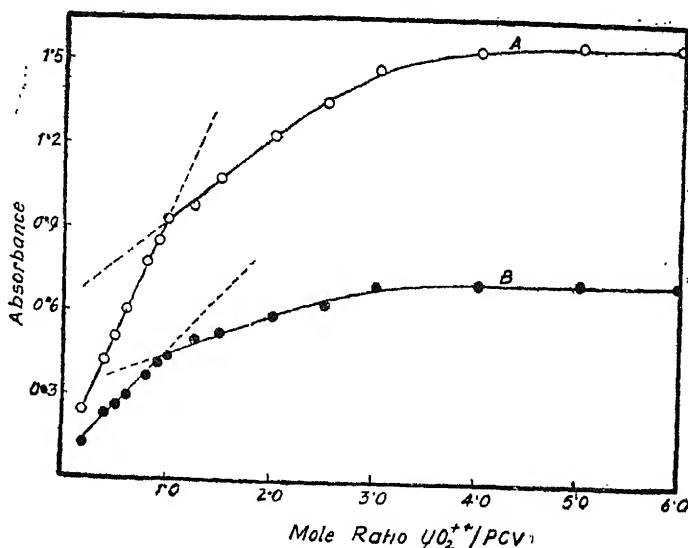


Fig. 4. Determination of chelate composition by mole ratio method at 600 m μ ; pH 6.5; Final concentration of PCV, curve A, 8.00×10^{-5} M, curve B, 4.00×10^{-5} M.

Stability constant of the chelate: The stability constant values of the chelate were evaluated by method of continuous variation using non-equimolar solutions (Fig. 5) and employing the following equation :

$$K = \frac{c^{(m+n-1)} p^{n-1} [(p m + n)x - n]^{m+n}}{m^{n-1} n^{m-1} (p-1)^{m+n-1} [n - (m+n)x]}$$

where

K = conditional stability constant

m = number of metal ions in the chelate

n = number of reagent molecules in the chelate

p = the ratio of the concentration of the reagent to the concentration of the metal ion.

x = mole fraction of the metal at absorption maximum.

and by mole ratio method (Fig. 4) employing the following expressions :

$$a = \frac{A_m - A_s}{A_m} \quad \text{and} \quad K = \frac{(m a c)^m (n a c)^n}{c(1-a)}$$

where

a = Degree of dissociation

A_m = maximum absorbance in the mole ratio plot

A_s = absorbance at the stoichiometric molar ratio in the mole ratio plot

m = number of metal ions in the chelate

n = number of reagent molecules in the chelate

c = final concentration of the reagent.

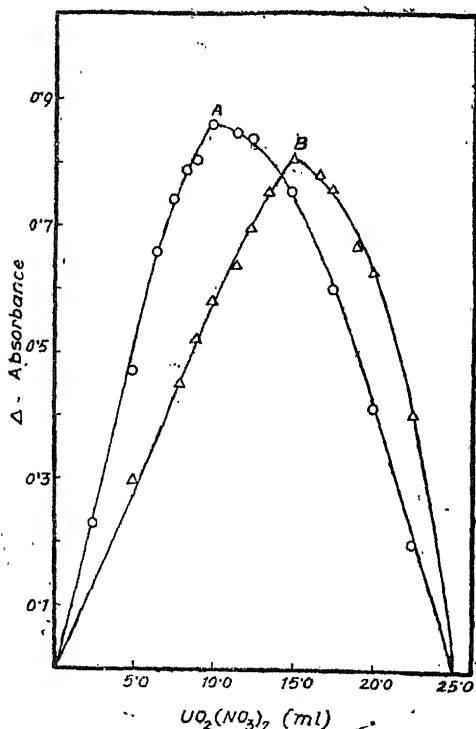


Fig. 5. Determination of chelate composition by method of continuous variation employing non-equimolar solutions at 600 m μ ; pH, 6.5; concentration of $\text{UO}_2(\text{NO}_3)_2$ and PCV, curve A, 2.00×10^{-4} M $\text{UO}_2(\text{NO}_3)_2$ and 1.00×10^{-4} M PCV, curve B, 1.00×10^{-4} M $\text{UO}_2(\text{NO}_3)_2$ and 2.00×10^{-4} M PCV.

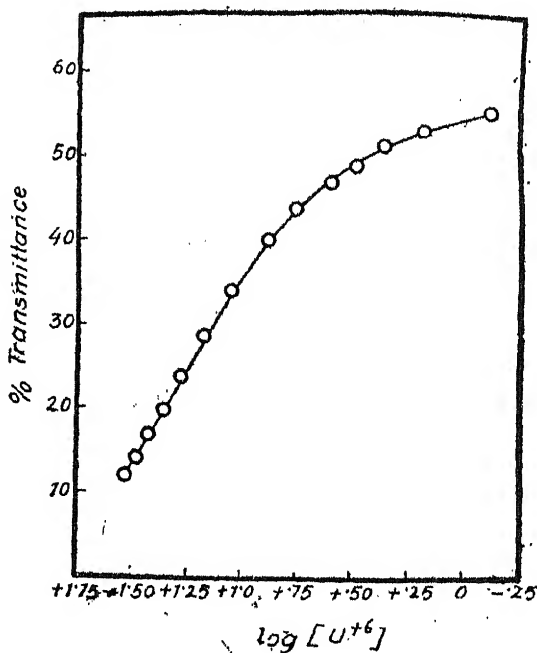


Fig. 6. Ringbom plot at 600 m μ .

The values of $\log K$ and corresponding ΔG° values have been summarised in the table below :

$\log K$ and ΔG° values of $U(IV) - PCV$ chelate
pH 6.5 ± 0.1 , Temperature $25^\circ C$

	Continuous variation method	Mole ratio Method
$\log K$	4.6	4.7
ΔG°	-6.3	-6.4

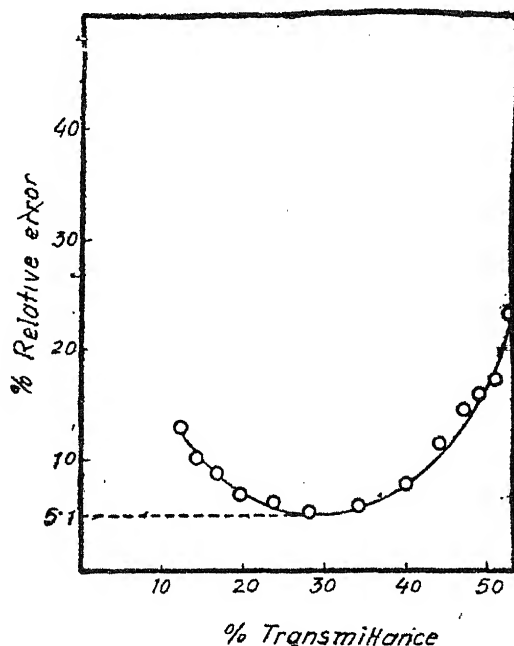


Fig. 7. Photometric error.

Beer's law range : The concentration range over which colour system obeys Beer's law is obtained by adopting the conventional method in which concentration of uranium is plotted against absorbance. The range of adherence to Lambert Bougort-Beer's law is found to be 34.3 to 0.8 ppm of uranium (VI) at 600 $m\mu$ and pH 6.5.

The Ringbom plot⁷ has also been obtained by plotting $\log [UO_2^{++}]$ vs % T (Fig. 6) and the concentration range corresponding to straight portion of the curve has been determined which is 30.5 to 3.8 ppm of uranium, which is the useful range over which accurate colorimetric analysis is possible. The relative

errors involved for different values of %*T* from the Ringbom plot are computed using Ayres⁸ equation and the results are represented graphically in Fig 7. It will be seen that the relative error is minimum when the transmittance is 30%.

Sensitivity of colour reaction : The sensitivity of colour reaction as defined by Sandell is 0.018 γ/cm^2 at 600 $m\mu$. The practical sensitivity corresponding to an absorbance change of 0.01 units is 0.18 γ/cm^2 .

Pyrocatechol violet is thus a sensitive chromogenic reagent for the micro determination of uranium (VI) when present singly and photometric analysis under suitable range of concentrations is possible.

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The Natural Number Arithmetic in Goedel's Axiomatic Set Theory

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Here the arithmetic of natural numbers has been introduced directly within Goedel's axiomatic set theory [1]. The operations of addition, multiplication and exponentiation have been defined on the basis of Goedel's theorem [1; sec. 8.5, p. 32]. Thus we start where Goedel stopped. In [1], Goedel constructed the class ω of natural numbers and derived the Peano axioms. The order relation among the natural numbers is a simple consequence of his definition of a natural number as an ordinal number. But the operations of addition, multiplication and exponentiation were not defined. Since Goedel's theory is thought of as a culmination of the axiomatic development which originated with Zermelo, it seems desirable to complete this arithmetic within Σ_1 . The approach here differs from the existing literature [*e.g.* 2] in details as well as in notation; our notation is a natural continuation and extension of [1].

Let i, k, l be variables over ω and σ the function [1; sec. 7.4, p. 26] such that if x is an ordinal number then $\sigma'x = x + \{x\}$. Let $0 = \Lambda$, the null set, $1 = \sigma'0$, $2 = \sigma'1$, $3 = \sigma'2$ etc., where $A'x$ denotes the value of a single-valued function A for the argument x . Then Goedel's theorem states:—

$T: \quad (a) \ (G) \ (\exists! F) \ [F \text{ Fn } \omega. \ \&. \ F'0 = a. \ \&. \ (k) \ (F'\sigma'k = G'F'k)].$

If $\lambda \text{ Fn } \omega$, then we call λ a sequence and if ω is the range of λ then we call λ a sequence of natural numbers.

ADDITION

In theorem T taking a to be a natural number i and specialising G to be σ , we have

Theorem A: $(i) \ (\exists! \lambda_i) \ [\lambda_i \text{ Fn } \omega. \ \&. \ \lambda_i'0 = i. \ \&. \ (k) \ (\lambda_i'\sigma'k = \sigma'\lambda_i'k)].$

Thus for each $i \in \omega$ we are assured of the existence and uniqueness of a sequence λ_i of naturals such that

- (1) $\lambda_i'0 = i$
- (2) $\lambda_i'\sigma'k = \sigma'\lambda_i'k$, for every $k \in \omega$.

Definition A: For every $i, k \in \omega$, $+ < i, k > = \lambda_i'k$.

Since $m(\omega)$ (*i.e.* ω is a set) we have also $m(\omega \times \omega)$ [1; 5.18, p. 18]. Hence $'+'$ is an operation on $\omega \times \omega$ to ω .

Theorem A α : For every $i, k \in \omega$,

- (1) $+ < i, \sigma'k > = \sigma' + < i, k >$
- (2) $+ < \sigma'i, k > = \sigma' + < i, k >$

Proof: (1) Definition A gives $+\langle i, \sigma'k \rangle = \lambda_i' \sigma'k$ and also $\sigma' + \langle i, k \rangle = \sigma' \lambda_i' k$.

Hence theorem A α (1) follows from theorem A(2).

(2) By definition A, we have, if $i \in \omega$, then for every $k \in \omega$

$$(i) + \langle \sigma' i, k \rangle = \lambda_{\sigma' i}' k \text{ and } (ii) \sigma' + \langle i, k \rangle = \sigma' \lambda_i' k.$$

By theorem A (1), if $i \in \omega$, we have (iii) $\lambda_{\sigma' i}' 0 = \sigma' i$ and by theorem A(2), we have (iv) $\lambda_{\sigma' i}' \sigma' k = \sigma' \lambda_{\sigma' i}' k$, for every $k \in \omega$. Again if $i \in \omega$, then by theorem A(1), (iii') $\sigma' \lambda_i' 0 = \sigma' i$, and by theorem A(2) (iv') $\sigma' \lambda_i' \sigma' k = \sigma' \sigma' \lambda_i' k$, for every $k \in \omega$.

On comparing (iii), (iv) to (iii'), (iv') respectively, we find that since the existence of a sequence for each $i \in \omega$ is unique by theorem A, we have $\lambda_{\sigma' i}' k = \sigma' \lambda_i' k$, for every $i, k \in \omega$. Hence the result follows from (i) and (ii).

Theorem A β for every $i \in \omega$,

$$(1) + \langle i, 0 \rangle = i$$

$$(2) + \langle 0, i \rangle = i$$

Hence for every $i \in \omega$, $+\langle i, 0 \rangle = + \langle 0, i \rangle$, i.e., 0 is the *identity* for the operation '+'.

Proof: (1) By definition A, $+\langle i, 0 \rangle = \lambda_i' 0$ for each $i \in \omega$ and by theorem A(1), $\lambda_i' 0 = i$ for each $i \in \omega$.

(2) By theorem A (1), $\lambda_0' 0 = 0$ and by theorem A (2), for each $i \in \omega$, $\lambda_0' \sigma' i = \sigma' \lambda_0' i = i$. But these properties are possessed by the sequence i . Hence $\lambda_0' i = i$. Since $+\langle 0, i \rangle = \lambda_0' i$ by definition A, we have $+\langle 0, i \rangle = i$.

Theorem A γ For every $i, k, l \in \omega$,

$$+ \langle + \langle i, k \rangle, l \rangle = + \langle i, + \langle k, l \rangle \rangle$$

This embodies the *associative law* for the operation '+'

Proof: Let $i, k \in \omega$. Let A be the class of naturals such that

$$(I) [l \in A \leftrightarrow + \langle + \langle i, k \rangle, l \rangle = + \langle i, + \langle k, l \rangle \rangle]$$

By theorem A β (1), we have $+\langle + \langle i, k \rangle, 0 \rangle = + \langle i, k \rangle$ and also $+\langle + \langle i, k \rangle, 0 \rangle = + \langle i, + \langle k, 0 \rangle \rangle$; hence (i) $0 \in A$.

Let $u \in A$, so that (ii) $+\langle + \langle i, k \rangle, u \rangle = + \langle i, + \langle k, u \rangle \rangle$.

Now $+\langle + \langle i, k \rangle, \sigma' u \rangle = \sigma' + \langle + \langle i, k \rangle, u \rangle$, by theorem A α (1)

$$= \sigma' + \langle i, + \langle k, u \rangle \rangle, \text{ by assumption (ii)}$$

$$= + \langle i, \sigma' + \langle k, u \rangle \rangle, \text{ by theorem A}\alpha(1)$$

$$\therefore (iii) + \langle + \langle i, k \rangle, \sigma' u \rangle = + \langle i, + \langle k, \sigma' u \rangle \rangle, \text{ by theorem A}\alpha(1).$$

Hence by (i), (ii) and (iii), we have $0 \in A$ & (u) $[u \in A \rightarrow \sigma' u \in A]$ and by the Principle of Induction [1; 8.44, p. 31], $\omega \subseteq A$. But by the definition of A , $A \subseteq \omega$. Thus $A = \omega$ and the theorem is proved.

Theorem A δ : For every $i, k \in \omega$, $+ < i, k > = + < k, i >$

This embodies the *commutative law* for the operation ' $+$ '

Proof : Let $i \in \omega$. Let A be the class of naturals such that

$$(k) [k \in A \leftrightarrow + < i, k > = + < k, i >].$$

By theorem A β , we have $+ < i, 0 > = + < 0, i >$. Hence (i) $0 \in A$. Let $u \in A$ so that (ii) $+ < i, u > = + < u, i >$.

We have $+ < i, \sigma^c u > = \sigma^c + < i, u >$, by theorem A α (1)
 $= \sigma^c + < u, i >$, by assumption (ii)

\therefore (iii) $+ < i, \sigma^c u > = + < \sigma^c u, i >$, by theorem A α (2)

Hence by (i), (ii) and (iii), $0 \in A$ & (u) $[u \in A \rightarrow \sigma^c u \in A]$ and by Principle of Induction, $\omega \subseteq A$. But by the definition of A , $A \subseteq \omega$. Thus $A = \omega$ and the theorem is proved.

Definition A' : $i + k = + < i, k > = \lambda_i 'k$, for every $i, k \in \omega$. This $\sigma^c i = \sigma^c \lambda_i '0 = \lambda_i ' \sigma^c 0 = \lambda_i '1 = i + 1$

Theorem A β , A γ and A δ may now be stated respectively as :

Theorem A' : (1) For every $i \in \omega$, $i + 0 = 0 + i = i$
 (2) For every $i, k, l \in \omega$, $(i + k) + l = i + (k + l)$
 (3) For every $i, k \in \omega$, $i + k = k + i$

Definition A'' : $i + k + l = (i + k) + l$ or $i + (k + l)$, for every $i, k, l \in \omega$.

MULTIPLICATION

In theorem T taking $F^c 0 = 0$ in place of $F^c 0 = a$, a to be a natural i , specialising G to be λ_i (of definition A) and replacing F by μ_i , we have

Theorem M : (i) $(\exists ! \mu_i) [\mu_i \text{ Fn } \omega \text{ \& } \mu_i '0 = 0 \text{ \& } (k) \mu_i ' \sigma^c k = \lambda_i ' \mu_i 'k]$,
 Thus for each $i \in \omega$, we are assured of the existence and uniqueness of a sequence μ_i of natural numbers such that

- (1) $\mu_i '0 = 0$
- (2) $\mu_i ' \sigma^c k = \lambda_i ' \mu_i 'k$, for each $k \in \omega$.

Definition M : For each $i, k \in \omega$, $\times < i, k > = \mu_i 'k$. The operation ' \times ' is defined on the set $\omega \times \omega$ to the set ω .

Theorem Ma : For every $i, k \in \omega$,

- (1) $\times < i, \sigma^c k > = \times < i, k > + i$
- (2) $\times < \sigma^c i, k > = \times < i, k > + k$

Proof : (1) By definition M , we have (i) $\times < i, \sigma^c k > = \mu_i ' \sigma^c k$ and by theorem A' (3), $\times < i, k > + i = i + \times < i, k >$ which by definition A' $= \lambda_i ' \times < i, k >$. Hence (ii) $\times < i, k > + i = \lambda_i ' \mu_i 'k$, by definition M . The result follows from (i), (ii) and theorem M (2).

(2) Let $i \in \omega$. Then by definition M , (i) for every $k \in \omega$, $\times \langle \sigma 'i, k \rangle = \mu_{\sigma 'i} 'k$. Also by theorem $A'(3)$, $\times \langle i, k \rangle + k = k + \times \langle i, k \rangle$ which is equal to $\lambda_k ' \times \langle i, k \rangle$, by definition A' . Hence by definition M , (ii) for every $k \in \omega$, $\times \langle i, k \rangle + k = \lambda_i ' \mu_i 'k$.

By theorem $M(1)$, we have (iii) for every $i \in \omega$, $\mu_{\sigma 'i} '0 = 0$ and by theorem $M(2)$, (iv) for every $i, k \in \omega$, $\mu_{\sigma 'i} ' \sigma 'k = \lambda_{\sigma 'i} ' \mu_{\sigma 'i} 'k$. Again by theorem $M(1)$, for every $i \in \omega$, $\lambda_0 ' \mu_i '0 = \lambda_i '0$ and by theorem $A(1)$, (iii') for every $i \in \omega$, $\lambda_0 ' \mu_i '0 = 0$.

$$\begin{aligned} \text{Also by theorem } M(2), \lambda_{\sigma 'i} ' \mu_i ' \sigma 'k &= \lambda_{\sigma 'i} ' \lambda_i ' \mu_i 'k \\ &= \lambda_{\sigma 'i} '(i + \mu_i 'k), \text{ by definition } A' \\ &= \sigma 'i + k + \mu_i 'k, \text{ by theorem } A'(3) \end{aligned}$$

Hence by definition A' , (iv') $\lambda_{\sigma 'i} ' \mu_i ' \sigma 'k = \lambda_{\sigma 'i} ' \lambda_i ' \mu_i 'k$, for every $i, k \in \omega$. On comparing (iii), (iv) to (iii'), (iv'), we find that since the existence of a sequence for each $i \in \omega$ is unique by theorem M , we have $\mu_{\sigma 'i} 'k = \lambda_i ' \mu_i 'k$, for every $i, k \in \omega$. The result follows from (i) and (ii).

Theorem $M\beta$: For every $i \in \omega$.

$$(a) (1) \times \langle i, 0 \rangle = 0$$

$$(2) \times \langle 0, i \rangle = 0$$

Hence $\times \langle i, 0 \rangle = \times \langle 0, i \rangle = 0$, for every $i \in \omega$.

$$(b) (1) \times \langle i, 1 \rangle = i$$

$$(2) \times \langle 1, i \rangle = i$$

Hence $\times \langle i, 1 \rangle = \times \langle 1, i \rangle = i$, for every $i \in \omega$.

i.e., 1 is the identity for the operation ' \times '.

Proof: (a) (1) by definition M , $\times \langle i, 0 \rangle = \mu_i '0$ and by theorem $M(1)$ $\mu_i '0 = 0$.

(2) By theorem $M(1)$, $\mu_0 '0 = 0$ and by theorem $M(2)$, $\mu_0 ' \sigma 'i = \lambda_0 ' \mu_0 'i$. Hence as in theorem $A\beta$, we have by definition M , $\times \langle 0, i \rangle = \mu_0 'i = 0$.

$$\begin{aligned} (b) (1) \text{ We have } \times \langle i, 1 \rangle &= \times \langle i, \sigma '0 \rangle \\ &= \times \langle i, 0 \rangle + i, \text{ by theorem } Ma(1) \\ &= 0 + i, \text{ by theorem } M\beta(a)(1) \end{aligned}$$

Hence $\times \langle 1, i \rangle = i$, by theorem $A'(1)$

$$(2) \times \langle 1, i \rangle = \times \langle \sigma '0, i \rangle = \times \langle 0, i \rangle + i, \text{ by theorem } Ma(2)$$

Hence by theorem $M\beta(a)(2)$, $\times \langle 1, i \rangle = 0 + i$

\therefore by theorem $A'(1)$, $\times \langle 1, i \rangle = i$.

Theorem M_γ : For every $i, k, l \in \omega$, $\times < i, k + l > = \times < i, k > + \times < i, l >$
This embodies the *distributive law* of the operation '×' over '+'.

Proof : Let $i, k \in \omega$. Let A be the class of naturals such that

$$(l) [l \in A \leftrightarrow \times < i, k + l > = \times < i, k > + \times < i, l >]$$

We have $\times < i, k + 0 > = \times < i, k >$, by theorem $A'(1)$
 $= \times < i, k > + 0$, by theorem $A'(1)$

Hence by theorem $M\beta$ (a) (1), $\times < i, k + 0 > = \times < i, k > + \times < i, 0 >$.
Thus (i) $0 \in A$.

Let $u \in A$, so that $\times < i, k + u > = \times < i, k > + \times < i, u > \dots (ii)$

Now, $\times < i, k + \sigma' u > = \times < i, k + (u + 1) >$
 $= \times < i, (k + u) + 1 >$, by theorem $A'(2)$
 $= \times < i, k + u > + i$, by theorem $Ma(1)$
 $= (\times < i, k > + \times < i, u >) + i$, by assumption (ii)
 $= \times < i, k > + (\times < i, u > + i)$, by theorem $A'(2)$

Hence $\times < i, k + \sigma' u > = \times < i, k > + \times < i, \sigma' u > \dots (iii)$, by theorem $Ma(1)$
Therefore, by (i), (ii) and (iii), we have $0 \in A$ & $(u) [u \in A \rightarrow \sigma' u \in A]$ and by the Principle of Induction $\omega \subseteq A$. But by the definition of A , $A \subseteq \omega$. Hence $A = \omega$ and the theorem is proved.

Theorem M_δ : For every $i, k, l \in \omega$, $\times < \times < i, k >, l > = \times < i, \times < k, l >$
This embodies the *associative law* for the operation '×'.

Proof : Let $i, k \in \omega$. Let A be the class of naturals such that

$$(l) [l \in A \leftrightarrow \times < \times < i, k >, l > = \times < i, \times < k, l > >]$$

We have $\times < \times < i, k >, 0 > = 0$, by theorem $M\beta$ (1). Hence by the same theorem $\times < \times < i, k >, 0 > = \times < i, \times < k, 0 > >$. Thus (i) $0 \in A$

Let $u \in A$ so that $\times < \times < i, k >, u > = \times < i, \times < k, u > > \dots (ii)$

Now $\times < \times < i, k >, \sigma' u > = \times < \times < i, k >, u > + \times < i, k >$, by theorem $Ma(1)$
 $= \times < i, \times < k, u > > + \times < i, k >$, by assumption (ii)
 $= \times < i, \times < k, u > + k >$, by theorem $M\gamma$.

Hence $\times < \times < i, k >, \sigma' u > = \times < i, \times < k, \sigma' u > >$, by theorem $Ma(1) \dots (iii)$

Hence by (i), (ii) and (iii), $0 \in A$ & $(u) [u \in A \rightarrow \sigma' u \in A]$

and by the Principle of Induction, $\omega \subseteq A$. But by the definition of A , $A \subseteq \omega$.
Hence $A = \omega$ and the theorem is proved.

Theorem M_ε : For every $i, k \in \omega$, $\times < i, k > = \times < k, i >$.

This embodies the *commutative law* for the operation '×'.

Proof: Let $i \in \omega$. Let A be the class of naturals such that

$$(k) [k \in A \leftrightarrow \times < i, k > = \times < k, i >].$$

We have $\times < i, 0 > = \times < 0, i >$ by theorem $M\beta(a)$ so that $(i) 0 \in A$.

Let $u \in A$ so that $\times < i, u > = \times < u, i > \dots (ii)$.

Now $\times < i, \sigma^c u > = \times < i, u > + i$, by theorem $Ma(1)$.

$$= \times < u, i > + i, \text{ by assumption (ii).}$$

Hence by theorem $Ma(2)$, we have $(iii) \times < i, \sigma^c u > = \times < \sigma^c u, i >$

Thus by (i) , (ii) and (iii) , $0 \in A$ & $(u) [u \in A \rightarrow \sigma^c u \in A]$ and by the Principle of Induction, $\omega \subseteq A$. But by the definition of A , $A \subseteq \omega$. Hence $A = \omega$ and the theorem is proved.

Definition M': $i \times k$ or $i \cdot k = \times < i, k > = \mu_i 'k$, for every $i, k \in \omega$.

Theorem $M\beta$ through Me may now be stated respectively as

Theorem M': (1) (a) For every $i \in \omega$, $i \times 0 = 0 \times i = 0$

$$(b) \text{ for every } i \in \omega, i \times 1 = 1 \times i = i$$

$$(2) \text{ For every } i, k, l \in \omega, i \times (k + l) = i \times k + i \times l$$

$$(3) \text{ For every } i, k, l \in \omega, i \times (k \times l) = (i \times k) \times l$$

$$(4) \text{ For every } i, k, l \in \omega, i \times k = k \times i$$

Definition M'': $i \cdot k \cdot l = (i, k) \cdot l$ or $i \cdot (k \cdot l)$ for every $i, k, l \in \omega$.

EXPONENTIATION

In theorem T , if we take $F'0 = 1$ in place of $F'0 = a$, μ_i (of definition M), in place of G , replace a by natural i and F by v_i , we have

Theorem E: $(i) (\exists! v_i) [v_i \in \omega \text{ \& } v_i '0 = 1 \text{ and } (k) (v_i ' \sigma^c k = \mu_i 'v_i 'k)]$

Hence for each $i \in \omega$, we are assured of the existence and uniqueness of a sequence v_i of naturals such that

$$(1) v_i '0 = 1$$

$$(2) v_i ' \sigma^c k = \mu_i 'v_i 'k, \text{ for every } k \in \omega.$$

Definition E. For every $i, k \in \omega$, $\wp < i, k > = v_i 'k$.

The operation ' \wp ' is defined on the set $\omega \times \omega$ to ω .

Theorem Ea: For every $i, k \in \omega$, $\wp < i, \sigma^c k > = \wp < i, k > \cdot i$

Proof: By definition E , $\wp < i, \sigma^c k > = v_i ' \sigma^c k \dots (i)$.

Also, $\wp < i, k > \cdot i = i \cdot \wp < i, k >$; by theorem $M'(4)$

$$= \mu_i ' \wp < i, k >, \text{ by theorem } M'.$$

Hence $\mathfrak{F} \langle i, k \rangle . i = \mu_i \text{ ' } v_i \text{ ' } k$, by definition $E \dots (ii)$

The result follows from (i) and (ii) and theorem $E(2)$

Theorem $E\beta$: For every $i \in \omega$.

$$(1) \mathfrak{F} \langle i, 0 \rangle = 1$$

$$(2) \mathfrak{F} \langle 0, i \rangle = 0$$

Proof: Let $i \in \omega$. We have $\mathfrak{F} \langle i, 0 \rangle = v_i \text{ ' } 0$ by definition E and $v_i \text{ ' } 0 = 1$ by theorem $E(1)$

(2) The proof is similar to that of theorem $A\beta$ (2).

Theorem $E\gamma$: For every $i, k, l \in \omega$, $\mathfrak{F} \langle i, k \rangle . \mathfrak{F} \langle i, l \rangle = \mathfrak{F} \langle i, k + l \rangle$

Proof: Let $i, k \in \omega$. Let A be the class of naturals such that

$$(l) [l \in A \leftrightarrow \mathfrak{F} \langle i, k \rangle . \mathfrak{F} \langle i, l \rangle = \mathfrak{F} \langle i, k + l \rangle].$$

We have $\mathfrak{F} \langle i, k \rangle . \mathfrak{F} \langle i, 0 \rangle = \mathfrak{F} \langle i, k \rangle . 1$, by theorem $E\beta(1)$

$$= \mathfrak{F} \langle i, k \rangle , \text{ by theorem } M'(1) (b)$$

Hence, $\mathfrak{F} \langle i, k \rangle . \mathfrak{F} \langle i, 0 \rangle = \mathfrak{F} \langle i, k + 0 \rangle$, by theorem $A'(1)$
so that $0 \in A \dots (i)$.

Let $u \in A$ so that $\mathfrak{F} \langle i, k \rangle . \mathfrak{F} \langle i, u \rangle = \mathfrak{F} \langle i, k + u \rangle \dots (ii)$.

Now $\mathfrak{F} \langle i, k \rangle . \mathfrak{F} \langle i, \sigma \text{ ' } u \rangle = \mathfrak{F} \langle i, k \rangle . \mathfrak{F} \langle i, u \rangle . i$, by theorem $E\alpha$

$$= \mathfrak{F} \langle i, k + u \rangle . i, \text{ by assumption } (ii)$$

$$= \mathfrak{F} \langle i, \sigma \text{ ' } (k + u) \rangle, \text{ by theorem } E\alpha.$$

Hence $\mathfrak{F} \langle i, k \rangle . \mathfrak{F} \langle i, \sigma \text{ ' } u \rangle = \mathfrak{F} \langle i, k + \sigma \text{ ' } u \rangle$, by theorem $A\alpha(1)$
and definition A' .

Thus by (i), (ii) and (iii), $0 \in A$. & (u) $[u \in A \rightarrow \sigma \text{ ' } u \in A]$

and by the Principle of Induction $\omega \subseteq A$. But by the definition of A , $A \subseteq \omega$.
Hence $A = \omega$ and the theorem is proved.

Theorem $E\delta$: For every $i, k, l \in \omega$, $\mathfrak{F} \langle \mathfrak{F} \langle i, k \rangle, l \rangle = \mathfrak{F} \langle i, k . l \rangle$.

Proof: Let $i, k \in \omega$. Let A be the class of naturals such that

$$(l) [l \in A \leftrightarrow \mathfrak{F} \langle \mathfrak{F} \langle i, k \rangle, l \rangle = \mathfrak{F} \langle i, k . l \rangle].$$

We have $\mathfrak{F} \langle \mathfrak{F} \langle i, k \rangle, 0 \rangle = 1$, by theorem $E\beta$ and also by theorem $M'(1) (a)$ $\mathfrak{F} \langle i, k . 0 \rangle = \mathfrak{F} \langle i, 0 \rangle$, which is $= 1$ by theorem $E\beta$.

Hence $0 \in A \dots (i)$

Let $u \in A$, so that $\mathfrak{F} \langle \mathfrak{F} \langle i, k \rangle, u \rangle = \mathfrak{F} \langle i, k . u \rangle \dots (ii)$.

Now, $\mathfrak{S} < \mathfrak{S} < i, k >, \sigma 'u > = \mathfrak{S} < \mathfrak{S} < i, k >, u >. \mathfrak{S} < i, k >, \text{ by theorem } E\alpha$
 $= \mathfrak{S} < i, k. u >. \mathfrak{S} < i, k >, \text{ by assumption (ii)}$
 $= \mathfrak{S} < i, k. u + k >, \text{ by theorem } E\gamma$
 $= \mathfrak{S} < i, k. u + k. 1 >, \text{ by theorem } M'(1) (b)$
 $= \mathfrak{S} < i, k. (u + 1) >, \text{ by theorem } M'(2).$

Hence $\mathfrak{S} < \mathfrak{S} < i, k >, \sigma 'u > = \mathfrak{S} < i, k. \sigma 'u > \dots (iii).$
 By (i), (ii) and (iii), $0 \in A$. & $(u) [u \in A \rightarrow \sigma 'u \in A]$ and by the Principle of Induction $\omega \subseteq A$. But by the definition of A , $A \subseteq \omega$. Hence $A = \omega$ and the theorem is proved.

Definition E' : $i^k = \mathfrak{S} < i, k >$

Theorem $E\beta$, $E\gamma$ and $E\delta$ may now be stated respectively as

Theorem $E(I)$ (a) $i^0 = 1$, for every $i \in \omega$.

(b) $0^i = 0$, for every $i \in \omega$.

(2) For every $i, k, l \in \omega$, $i^k. i^l = i^{k+l}$

(3) For every $i, k, l \in \omega$, $(i^k)^l = i^{k \cdot l}$

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On Maximal Subgroups and Direct Products of Groups

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1. Here we adopt the usual terminology and notations.

We have the following propositions :

Prop. 1. The limit of a properly ascending sequence of subgroups of a given group G cannot be finitely generated [1]

Prop. 2. If $G = A_1 \times \dots \times A_n (= \prod_{i=1}^n A_i)$ is a direct product of groups A_1, \dots, A_n , then G is finitely generated if and only if each A_i is finitely generated.

In fact, if y_i is a generator of A_i , $i = 1, \dots, n$, then $y = \bar{y}_1 U \dots U \bar{y}_n$ is a generator of G , where $\bar{y}_i = \{e_1\} \times \dots \times \{e_{i-1}\} \times y_i \times \{e_{i+1}\} \times \dots \times \{e_n\}$, e_i being the identity of A_i and y_i occupying the i th place in the direct product.

Prop. 3. A group G satisfies the maximal condition if and only if G and each subgroup of G are finitely generated.

2. It is known [3] that a finitely generated group G may have an infinitely generated subgroup.

Theorem 1. In every finitely generated group G which contains an infinitely generated subgroup K , there exists a maximal infinitely generated subgroup M of G (i. e. a subgroup which is maximal among infinitely generated subgroups).

Proof: If K itself is maximal, then we take $K = M$; if not, then we have an ascending sequence of distinct subgroups of G :

$$K \subset K_1 \subset \dots \subset K_n \subset \dots$$

such that each subgroup is infinitely generated. If the sequence is finite and terminates with $n = m$, say, then K_m is the desired maximal. If the sequence is infinite, let the limit of the sequence be denoted by H . Since, G is finitely generated and H is infinitely generated (Prop. 1), $H \neq G$. We take $H = M$.

Remark: If G is infinitely generated and contains an infinitely generated proper subgroup K , then M will coincide with G .

Theorem 2. No finitely generated subgroup of an infinitely generated group G can be maximal.

Thus if G is infinitely generated, then every maximal subgroup of G is infinitely generated.

Proof: Let H be any subgroup of G , which is finitely generated. Let $H = \{a_1, \dots, a_n\}$ where $a_1, \dots, a_n \in G$. Since, H is finitely generated $G \neq H$. If $b \in G - H$, then $\langle H, b \rangle$ the subgroup generated by H and b , contains H as a subgroup and is finitely generated by a_1, \dots, a_n, b . But, $\langle a_1, \dots, a_n, b \rangle \neq G$, since G is infinitely generated. Hence H is not maximal.

Corollary. If any maximal proper subgroup of a group G is finitely generated, then G is finitely generated.

3. Now, consider $G = \prod_{i=1}^n A_i$, where A_i is a group, $i = 1, \dots, n$. Let e_i denote the identity of A_i . Then $(e_1; \dots, e_{i-1}, a_i, e_{i+1}, \dots, e_n) \in A_i$ where a_i occupies the i th place in the n -tuple. Let $(a_1, \dots, a_n) \in G$. Then $(a_1, \dots, a_n) = (a_1, e_2, \dots, e_n)(e_1, a_2, e_3, \dots, e_n) \dots (e_1, e_2, \dots, e_{n-1}, a_n)$. Thus

$$(a_1, \dots, a_n) \in \left\{ \bigcup_{i=1}^n A_i \right\}$$

Hence $G \subseteq \left\{ \bigcup_{i=1}^n A_i \right\}$. Also any element of $\left\{ \bigcup_{i=1}^n A_i \right\}$ is an element of G .

Hence $\left\{ \bigcup_{i=1}^n A_i \right\} \subseteq G$ Hence $G = \left\{ \bigcup_{i=1}^n A_i \right\}$ Thus follows

Theorem 3. If $G = \prod_{i=1}^n A_i$, where A_i is a group, then the group $\left\{ \bigcup_{i=1}^n A_i \right\}$ is the whole group G and is, therefore, the only maximal subgroup containing all of A_1, \dots, A_n as subgroups.

Theorem 4. If H is a subgroup of $G = \prod_{i=1}^n A_i$, then there is a subgroup H_i of A_i ($i = 1, \dots, n$) such that $H \subseteq \prod_{i=1}^n H_i$

Proof. Let H_i be the set of the i th members of the n -tuples in H , $i = 1, \dots, n$. Since H is a group, each H_i will be a group under the operation which makes A_i a group and $H_i \subseteq A_i$ $i = 1, \dots, n$. Hence $H \subseteq H_1 \times \dots \times H_n$.

We shall now consider a maximal proper subgroup of $G = \prod_{i=1}^n A_i$, which contains some but not all of A_1, \dots, A_n , in this order. We shall investigate the case in which none of A_1, \dots, A_n is an identity group.

Suppose M is a subgroup of G , containing A_1, \dots, A_l as subgroups but not containing A_{l+1}, \dots, A_n . Then M will contain $A_1, U \dots U A_l$. Hence according to theorem 3, M will contain $A_1 \times \dots \times A_l$ as a proper subgroup.

If we consider all the n -tuples $(x_1, \dots, x_l, x_{l+1}, \dots, x_n) \in G$ then the set of all n tuples $(x_1, \dots, x_l, e_{l+1}, \dots, e_n)$ will form a proper subgroup of G , which we denote by A' ; $A' = A_1 \times \dots \times A_l$. The set of all n -tuples $(e_1, \dots, e_l, x_{l+1}, \dots, x_n)$ will also form a proper subgroup of G , which we denote by B^l and which equals $A_{l+1} \times \dots \times A_n$. We have $A' \subseteq M \subseteq G$ (1) where $X \subseteq Y$ denotes that the group X is a proper subgroup of Y .

The set $\{(y_1, \dots, y_l, e_{l+1}, \dots, e_n) \mid (y_1, \dots, y_n) \in M\}$ will form a subgroup of M . This subgroup will be coincident with A' by virtue of (1). The set $\{(e_1, \dots, e_l, y_{l+1}, \dots, y_n) \mid (y_1, \dots, y_n) \in M\}$ will form a proper subgroup, say K , of B^l . Thus $A' \times K$ will be a proper subgroup of $A' \times B^l (= G)$ and M is a subgroup of $A' \times K$ (Theorem 4). Thus (1) extends to

$$A^l \subseteq M \subseteq A^l \times K \subseteq G \quad (2)$$

where

$$K \subseteq B^l \quad (3)$$

If M is a maximal subgroup of G , then we must have $M = A^l \times K$ (4)

We conclude that K must be a maximal proper subgroup of B^l . For, if not, B^l will contain a proper subgroup K_1 such that $K \subseteq K_1$. Then $A^l \times K \subseteq A^l \times K_1$ contradicting that M is maximal.

Conversely, if K is a maximal proper subgroup of B^l , then obviously $A^l \times K$ will be a maximal proper subgroup of G , containing A^l as a subgroup.

Hence we have

Theorem 5. A subgroup M of $A_1 \times \dots \times A_n$, containing A_1, \dots, A_l as subgroups but not A_{l+1}, \dots, A_n is a maximal proper subgroup of $A_1 \times \dots \times A_n$ if and only if $M = A^l \times K$, where $A^l = A_1 \times \dots \times A_l$ and K is a maximal proper subgroup of $B^l = A_{l+1} \times \dots \times A_n$.

Theorem 6. If $G = \bigtimes_{i=1}^n A_i$ satisfies the maximal condition, then each A_i will

also satisfy the maximal condition.

Proof. Since G satisfies the maximal condition, G and each subgroup of G are finitely generated (Prop. 3). Hence each of A_1, \dots, A_i is finitely generated (Prop. 2). Now, in order that A_i ($i = 1, \dots, n$) satisfies the maximal condition, it suffices to show that each subgroup of A_i ($i = 1, \dots, n$) is finitely generated.

If possible, suppose that there is some A_i , say A_m such that some subgroup of A_m , say A_{ms} is not finitely generated. Consider now any subgroups $G_1, \dots, G_{m-1}, G_{m+1}, \dots, G_n$ of $A_1, \dots, A_{m-1}, A_{m+1}, \dots, A_n$ respectively. Then $G_1 \times \dots \times G_{m-1} \times A_{ms} \times G_{m+1} \times \dots \times G_n$ is not finitely generated, (Prop. 2), although it is a subgroup of G thus violating the hypothesis that G satisfies the maximal condition. Hence A_i ($i = 1, \dots, n$) satisfies the maximal condition.

4. We note the following questions :

Q. 1. Does there exist a group G which satisfies neither the maximal condition nor the minimal condition ?

Q. 2. Does there exist a group G containing an ascending chain (of distinct subgroups) of the type $H_1 \subseteq \dots \subseteq H_n \subseteq \dots \subseteq H_w \subseteq H_{w+1} \subseteq \dots \subseteq H_{w_2} \subseteq \dots \subseteq G$, where w is the initial number of the second number class of ordinals ?

Q. 3. Does there exist an uncountable group which is the limit of a properly ascending sequence of subgroups ?

Questions of this nature do not seem to have been formulated and answered before. The formation of direct products is a technique by means of which constructions can be effected to answer such questions.

Let (A_i) be an indexed set of groups, where $i \in I$ and I is the set of integers. Arrange A_i according to the increasing order of $i \in I$.

Let $G = \bigtimes_{i \in I} A_i \left(= \bigtimes_{i=-\infty}^{\infty} A_i \right)$ denote the group which is the generalized direct product of $A_i, i \in I$.

Then

$$\dots \supseteq \bigcup_{i=-1}^{\infty} A_i \supseteq \bigcup_{i=0}^{\infty} A_i \supseteq \bigcup_{i=1}^{\infty} A_i \supseteq \dots$$

is an infinite chain of distinct subgroups of G . It provides an infinite ascending chain of distinct subgroups of G , which is at the same time an infinite descending chain of distinct subgroups of G . Consequently G does satisfy neither the maximal condition nor the minimal condition. This answers question 1 in the affirmative.

Consider the following chain of distinct groups.

$$\begin{aligned} A_1 &\subseteq A_1 \times A_2 \subseteq A_1 \times A_2 \times A_3 \subseteq \dots \subseteq \bigcup_{i=1}^{\infty} A_i \subseteq \left(\bigcup_{i=1}^{\infty} A_i \right) \times A_1 \\ &\subseteq \left(\bigcup_{i=1}^{\infty} A_i \right) \times A_1 \times A_2 \subseteq \dots \subseteq \left(\bigcup_{i=1}^{\infty} A_i \right) \times \left(\bigcup_{i=1}^{\infty} A_i \right) \subseteq \dots, \end{aligned}$$

where the groups appearing in the chain before any step are (normal) subgroups of the group at that step, e.g., $A_1, A_1 \times A_2$ are the subgroups of $A_1 \times A_2 \times A_3$. This answers question 2 in the affirmative.

Let A_i ($i \in I$), where I is the set of positive integers, be groups, each of order 2. Then the limit of the sequence of distinct subgroups,

$$A_1 \subseteq A_1 \times A_2 \subseteq \dots \subseteq \bigcup_{i=1}^n A_i \subseteq \dots$$

is the group $\bigcup_{i=1}^{\infty} A_i$, which

is of order $2^{\aleph_0} = \aleph$. This answers question 3 in the affirmative.

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A note on Zeros of the transcendental function $\{\nu + f(z)\} J_\nu(z) - z J_{\nu+1}(z)$ associated with an odd function $f(z)$

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Abstract

Previously we have determined the Zeros of the transcendental function $\{\nu + f(z)\} J_\nu(z) - z J_{\nu+1}(z)$ associated with the even function $f(z)$, and obtained certain results in connection with the same.

In the present paper similar results have been obtained in the case of the transcendental function

$$H_\nu(z) \equiv \{\nu + f(z)\} J_\nu(z) - z J_{\nu+1}(z)$$

associated with the odd function $f(z)$; in view of the fact that the zeros are unsymmetrically situated with respect to the origin.

1. Introduction

Previously⁽¹⁾ we have established certain results concerning the zeros of the transcendental function

$$G_\nu(z) \equiv \{\nu + f(z)\} J_\nu(z) - z J_{\nu+1}(z), \quad (1.1)$$

when $f(z)$ is an even function of z , by the application of the method due to Euler and Rayleigh⁽²⁾.

In the present paper similar results have been obtained for the function

$$H_\nu(z) \equiv \{\nu + f(z)\} J_\nu(z) - z J_{\nu+1}(z), \quad (1.2)$$

when $f(z)$ is an odd function with the addition that $f(z)$ is bounded for all z .

Unlike the previous case, we have started with the assumption that the positive and negative zeros of $H_\nu(z)$ are unsymmetrically situated with respect to the origin, and thus attempted to put forward a method to obtain the real zeros of $H_\nu(z)$, given under 4 and 6 of the present paper.

In the end, smallest positive and negative zeros $g_{0,1}$ and $-h_{0,1}$ of the function $\frac{1}{z} H_0(z)$ when $f(z) = z$ have been determined, as given by Tables I and II under 7a.

2. Number of zeros of $H_\nu(z)$ in an assigned strip of the Z-plane :

Obviously, the function $H_\nu(z)$ is bounded for large values of $|z|$ when $f(z)$ is bounded.

Hence the integral $\frac{1}{2\pi i} \int_C \frac{d}{dz} \log \{z^{-\nu} H_\nu(z)\} dz$ taken along the sides of the

rectangle C with its vertices $\pm i \{B + \frac{\pi}{2} I(\nu)\}$, $\pm iB + m\pi + \frac{\nu\pi}{2} + \frac{1}{4}\pi$ for large values of B and large integral values of m , is equal to the total number of zeros of $H_\nu(z)^{(1)}$.

It can be shown further by using the method applied to $G_\nu(z)$ when $f(z)$ is an even function of $z^{(1)}$, that the number of zeros of $H_\nu(z)$ associated with an odd function $f(z)$, between the imaginary axis and the line on which $R(z) = m\pi + \frac{\pi}{2} R(\nu) + \frac{1}{4}\pi$, is precisely equal to m .

3. Regions for the zeros of $H_\nu(z)$:

Obviously, the equations $H_\nu(g_{\nu,i}) = 0$, and $H_\nu(-h_{\nu,i}) = 0$, give an idea that $g_{\nu,i} \neq h_{\nu,i}$ for all positive integral values of i , by virtue of the result

$$H_\nu(-z) = (-1)^\nu \{H_\nu(z) - 2f(z)J_\nu(z)\} \quad (3.1)$$

and hence we conclude that the zeros $g_{\nu,i}$ and $-h_{\nu,i}$ lie unsymmetrically with respect to the origin inside the rectangle whose angular points are $\pm iB + \frac{\pi}{2} I(\nu)$ $\pm \{m\pi + \frac{\pi}{2} R(\nu) + \frac{1}{4}\pi\}$.

4. Infinite product for $H_\nu(z)$:

We shall begin with the assumption that $H_\nu(g_{\nu,i}) = 0$, and $H_\nu(-h_{\nu,i}) = 0$, $g_{\nu,i} \neq h_{\nu,i}$ for all positive integral values of i , such that $g_{\nu,i} \neq g_{\nu,j}$ and $h_{\nu,i} \neq h_{\nu,j}$ for all $i \neq j$; with the addition that

$$\frac{R}{I}(g_{\nu,i}, h_{\nu,i}) < \frac{R}{I}(g_{\nu,j}, h_{\nu,j}) \text{ for all } i \text{ and } j \text{ satisfying } 0 < i < j.$$

$$\text{Obviously, the integral } \frac{1}{2\pi i} \int_D \frac{1}{w-z} \frac{d}{dw} \log \{w^{-\nu} H_\nu(w)\} dw \quad (4.1)$$

taken along the rectangle D with vertices $\pm A \pm iB$ for large values of A and B , may be evaluated with respect to the poles $z, g_{\nu,i}$ and $-h_{\nu,i}$ for all $i = 1, 2, \dots, m$,

$$\begin{aligned} &\text{in the form} \quad \frac{1}{2\pi i} \int_D \frac{1}{w-z} \frac{d}{dw} \log \{w^{-\nu} H_\nu(w)\} dw \\ &= \frac{d}{dz} \log \{z^{-\nu} H_\nu(z)\} + \sum_{i=1}^m \frac{1}{g_{\nu,i}-z} - \sum_{i=1}^m \frac{1}{z+h_{\nu,i}} \end{aligned} \quad (4.2)$$

Again, since $\frac{d}{dw} \log \{w^{-\nu} H_\nu(w)\}$ is bounded inside and upon the rectangle D , we observed that

$$\frac{1}{2\pi i} \int_D \frac{1}{w-z} \frac{d}{dw} \log \{w^{-\nu} H_\nu(w)\} dw \rightarrow 0 \quad (4.3)$$

Thus, we have

$$\frac{d}{dz} \log \{z^{-\nu} H_\nu(z)\} = \sum_{i=1}^m \frac{1}{z+h_{\nu,i}} - \sum_{i=1}^m \frac{1}{g_{\nu,i}-z} \quad (4.4)$$

Taking 'm' to be indefinitely large, which is easily justified by virtue of 2, we find

$$\frac{d}{dz} \log \{z^{-\nu} H_{\nu}(z)\} = \sum_{i=1}^{\infty} \frac{1}{z+h_{\nu,i}} - \sum_{i=1}^{\infty} \frac{1}{g_{\nu,i}-z} \quad (4.5)$$

Integrating with respect to z , between the limits $(0, z)$, we get

$$H_{\nu}(z) = \left\{ \frac{\nu+f(0)}{\Gamma(\nu+1)} \right\} (z/2)^{\nu} \prod_{i=1}^{\infty} \left(1 - \frac{z}{g_{\nu,i}} \right) \left(1 + \frac{z}{h_{\nu,i}} \right) \quad (4.6)$$

5. Limitations of $\frac{d}{dz} \log \{z^{-\nu} H_{\nu}(z)\}$ when $|z|$ is large

Obviously,
$$\left| \frac{d}{dz} \log \{z^{-\nu} H_{\nu}(z)\} \right| = \left| \frac{\{\nu-f(z)\} J_{\nu+1}(z) + \{f'(z)-z\} J_{\nu}(z)}{\{\nu+f(z)\} J_{\nu}(z) - z J_{\nu+1}(z)} \right|$$
$$= \left| 1 + \frac{\{\nu-f(z)\} J_{\nu+1}(z)}{\{f'(z)-z\} J_{\nu}(z)} / \frac{\{\nu+f(z)\} J_{\nu}(z)}{\{f'(z)-z\} J_{\nu}(z)} - \frac{z J_{\nu+1}(z)}{\{f'(z)-z\} J_{\nu}(z)} \right|$$
$$\leq 1 + \left| \frac{\nu-f(z)}{f'(z)-z} \right| \left| \frac{J_{\nu+1}(z)}{J_{\nu}(z)} \right| / \left| \frac{z}{f'(z)-z} \right| \left| \frac{J_{\nu+1}(z)}{J_{\nu}(z)} \right| - \left| \frac{\nu+f(z)}{f'(z)-z} \right| \quad (5.1)$$

Hence the bounds of $\frac{d}{dz} \log \{z^{-\nu} H_{\nu}(z)\}$ are dependent upon the bounds of $J_{\nu+1}(z)/J_{\nu}(z)$.

Again, by virtue of the result⁽³⁾,

$$J_{\nu}(z) \sim (2/\pi z)^{\frac{1}{2}} \left[\{1+\eta_{1,\nu}(z)\} e^{i(z-\frac{\nu\pi}{2}-\frac{\pi}{4})} + \{1+\eta_{2,\nu}(z)\} e^{-i(z-\frac{\nu\pi}{2}-\frac{\pi}{4})} \right]$$

for large values of $|z|$, we find

$$\left| J_{\nu+1}(z)/J_{\nu}(z) \right| < \frac{1}{2} \left\{ \frac{1-2 \left| e^{2i(z-\frac{\nu\pi}{2}-\frac{\pi}{4})} \right|}{1+2 \left| e^{2i(z-\frac{\nu\pi}{2}-\frac{\pi}{4})} \right|} \right\} \text{ or } \frac{1}{2} \left\{ \frac{\frac{1}{2} \left| e^{2i(z-\frac{\nu\pi}{2}-\frac{\pi}{4})} \right| - 1}{1+2 \left| e^{2i(z-\frac{\nu\pi}{2}-\frac{\pi}{4})} \right|} \right\}$$

$$\text{according as } \left| e^{2i(z-\frac{\nu\pi}{2}-\frac{\pi}{4})} \right| < \frac{1}{2} \text{ or } > 2, \quad (5.2)$$

provided that each of the functions $\eta_{1,\nu}(z)$, $\eta_{1,\nu+1}(z)$, $\eta_{2,\nu}(z)$ and $\eta_{2,\nu+1}(z)$ is less than 1/4 in absolute value.

Therefore the bounds of $\frac{d}{dz} \log \{z^{-\nu} H_{\nu}(z)\}$ lie on the sides $R(z) = \pm(m\pi + \frac{\pi}{2} R(\nu) + \frac{1}{4} \pi)$, $I(\nu) = \pm \{ \frac{\pi}{2} I(\nu) + y \}$; $|y| \leq B$, of the rectangle D , subject to the restriction that

$$\left| e^{2i(z-\frac{\nu\pi}{2}-\frac{\pi}{4})} \right| > \text{Max} \left[2, \frac{1+2 \left| \frac{\nu+f(z)}{z} \right|}{\frac{1}{2}-4 \left| \frac{\nu+f(z)}{z} \right|} \right] \quad (5.3)$$

$$\text{or} \quad \left| e^{zi} (z^{-\frac{\nu\pi}{2} - \frac{\pi}{4}}) \right| < \text{Min} \left[\frac{1}{2}, \frac{1-2 \left| \frac{\nu+f(z)}{z} \right|}{2+4 \left| \frac{\nu+f(z)}{z} \right|} \right] \quad (5.4)$$

5a. Special cases :

(i) In particular if $f(z) = h$ (Constant), (5.3) and (5.4) assume the forms

$$\left| e^{zi} (z^{-\frac{\nu\pi}{2} - \frac{\pi}{4}}) \right| > \text{Max} \left[2, \frac{1+2 \left| \frac{h+\nu}{z} \right|}{\frac{1}{2}-4 \left| \frac{h+\nu}{z} \right|} \right]$$

$$\text{or} \quad \left| e^{zi} (z^{-\frac{\nu\pi}{2} - \frac{\pi}{4}}) \right| < \text{Min} \left[\frac{1}{2}, \frac{1-2 \left| \frac{h+\nu}{z} \right|}{2+4 \left| \frac{h+\nu}{z} \right|} \right],$$

which was established previously⁽⁴⁾.

(ii) In particular, if $f(z) = z$, $\nu = 0$, we arrive at the result that the bounds of the function $z\{J_0(z) - J_1(z)\}$ lie in the region, defined by the inequalities

$$\left| e^{zi} (z - \frac{\pi}{4}) \right| > \text{Max} [2, -\frac{6}{7}] > 2 \quad (5a.1)$$

$$\text{or} \quad \left| e^{zi} (z - \frac{\pi}{4}) \right| < \text{Min} [\frac{1}{2}, -\frac{1}{6}] < -\frac{1}{6} \quad (5a.2)$$

6. Determination of σ - numbers corresponding to the function $H_\nu(z)$.

By virtue of (4.4), we find that

$$\frac{d}{dz} \log \{z^{-\nu} H_\nu(z)\} = \sum_{i=1}^{\infty} \frac{1}{h_{\nu,i}} \left(1 + \frac{z}{h_{\nu,i}}\right)^{-1} - \sum_{i=1}^{\infty} \frac{1}{g_{\nu,i}} \left(1 - \frac{z}{g_{\nu,i}}\right)^{-1}$$

$$\text{or} \quad \frac{d}{dz} \log \{z^{-\nu} H_\nu(z)\} = - \sum_{m=0}^{\infty} z^m \left\{ \sigma_{\nu,1}^{(m+1)} + (-1)^{m+1} \sigma'_{\nu,1}{}^{(m+1)} \right\} \quad (6.1)$$

$$\text{where} \quad \sigma_{\nu,1}^{(m)} = \sum_{i=1}^{\infty} 1/g_{\nu,i}^m \text{ and } \sigma'_{\nu,1}{}^{(m)} = \sum_{i=1}^{\infty} 1/h_{\nu,i}^m.$$

Substituting the value of $H_\nu(z)$, as obtained from (1.1); (6.1) may be cast into the form

$$\begin{aligned} \{\nu - f(z)\} J_{\nu+1}(z) + \{f'(z) - z\} J_\nu(z) &= [z J_{\nu+1}(z) - \{\nu + f(z)\} J_\nu(z)] \times \\ &\sum_{m=0}^{\infty} z^m \left\{ \sigma_{\nu,1}^{(m+1)} + (-1)^{m+1} \sigma'_{\nu,1}{}^{(m+1)} \right\} \end{aligned} \quad (6.2)$$

Replacing $f(z)$ by a known odd function and comparing various powers of z , σ -numbers may be calculated in the forms $\sigma_{\nu,1}^{(2p)} + \sigma'_{\nu,1}^{(2p)}$ and

$$\sigma_{\nu,1}^{(2p+1)} - \sigma'_{\nu,1}^{(2p+1)}, \text{ where } p \text{ is zero or a positive integer.}$$

7. Idea of the existence of real zeros of $H_\nu(z)$:

We have seen previously⁽⁴⁾, that the real positive zeros $g_{\nu,i}$ and $h_{\nu,i}$, obtained from the relations $\sigma_{\nu,i}^{(m)} = \sum_{p=i}^{\infty} 1/g_{\nu,p}^m$ and $\sigma'_{\nu,i}^{(m)} = \sum_{p=i}^{\infty} 1/h_{\nu,p}^m$ ($m \equiv$ positive integer), satisfy the inequalities

$$\left[\sigma_{\nu,i}^{(m)} \right]^{-1/m} < g_{\nu,i} < \sigma_{\nu,i}^{(m)} / \sigma_{\nu,i}^{(m+1)} \quad (7.1)$$

$$\text{and} \quad \left[\sigma'_{\nu,i}^{(m)} \right]^{-1/m} < h_{\nu,i} < \sigma'_{\nu,i}^{(m)} / \sigma'_{\nu,i}^{(m+1)} \quad (7.2)$$

provided that $g_{\nu,i} < g_{\nu,j}$ and $h_{\nu,i} < h_{\nu,j}$ for all positive integral values of i and j satisfying $0 < i < j$.

Combining (7.1) and (7.2), we get

$$\sigma_{\nu,i}^{(m)} + \sigma'_{\nu,i}^{(m)} > \sigma_{\nu,i}^{(m)} \quad \text{or} \quad \sigma'_{\nu,i}^{(m)} \quad (7.3)$$

$$\text{or} \quad \sigma_{\nu,i}^{(m)} + \sigma'_{\nu,i}^{(m)} > \frac{1}{g_{\nu,i}^m} \quad \text{or} \quad \frac{1}{h_{\nu,i}^m} \quad (7.4)$$

Again, assuming $h_{\nu,i} > g_{\nu,i}$, we find that

$$\begin{aligned} \sigma_{\nu,i}^{(m+1)} - \sigma'_{\nu,i}^{(m+1)} &< \sigma_{\nu,i}^{(m+1)} + \sigma'_{\nu,i}^{(m+1)} < \left\{ \frac{\sigma_{\nu,i}^{(m)}}{g_{\nu,i}} + \frac{\sigma'_{\nu,i}^{(m)}}{h_{\nu,i}} \right\} \\ &< \frac{1}{g_{\nu,i}} \left\{ \sigma_{\nu,i}^{(m)} + \sigma'_{\nu,i}^{(m)} \right\} \end{aligned}$$

$$\text{or} \quad g_{\nu,i} < \frac{\sigma_{\nu,i}^{(m)} + \sigma'_{\nu,i}^{(m)}}{\sigma_{\nu,i}^{(m+1)} - \sigma'_{\nu,i}^{(m+1)}}, \quad (7.5)$$

provided that $\sigma_{\nu,i}^{(m)} > \sigma'_{\nu,i}^{(m)}$ for positive integral values of m .

Thus, we have

$$\left[\sigma_{\nu,i}^{(m)} + \sigma'_{\nu,i}^{(m)} \right]^{-1/m} < g_{\nu,i} < \left[\sigma_{\nu,i}^{(m)} + \sigma'_{\nu,i}^{(m)} \right] \sigma_{\nu,i}^{(m+1)} - \sigma'_{\nu,i}^{(m+1)} \quad (7.6)$$

Also, by virtue of the inequality $\sigma_{\nu,i}^{(m)} > \sigma'_{\nu,i}^{(m)}$ we find

$$\sigma_{\nu,i}^{(m)} + \sigma'_{\nu,i}^{(m)} > 2 \sigma'_{\nu,i}^{(m)} > \frac{2}{h_{\nu,i}^{(m)}}$$

$$\text{or} \quad h_{\nu,i} > \left[\frac{\sigma_{\nu,i}^{(m)} + \sigma'_{\nu,i}^{(m)}}{2} \right]^{-1/m} \quad (7.7)$$

Giving successive values to ' m ', the difference between the numbers

$$\left[\sigma_{\nu,i}^{(m)} + \sigma'_{\nu,i}^{(m)} \right]^{-1/m} \text{ and } \sigma_{\nu,i}^{(m)} + \sigma'_{\nu,i}^{(m)} \left| \sigma_{\nu,i}^{(m+1)} - \sigma'_{\nu,i}^{(m+1)} \right|$$

can be made as small as we please ; which ultimately gives rise to a process for calculating the zeros $g_{\nu,i}$. It may, however, be mentioned that the idea of the zeros $h_{\nu,i}$ can be framed out from the inequality (7.7) and the value may be obtained from the tables of Bessel functions.

We shall now present an example in support of the above idea.

7a. Example. Smallest zero of $H_0(z) \equiv z \cdot J_0(z) - J_1(z)$

Replacing $H_\nu(z)$ by $\frac{1}{z} H_\nu(z)$ and putting $\nu=0$, (6.2) assumes the form

$$\frac{1}{2} J_2(z) - \frac{1}{2} J_0(z) - J_1(z) = [J_1(z) - J_0(z)] \sum_{m=0}^{\infty} z^m \left\{ \sigma_{0,1}^{(m+1)} + (-1)^{m+1} \sigma'_{0,1}^{(m+1)} \right\} \quad (7a.1)$$

Comparing the various powers of ' z ', we get

$$\sigma_{0,1}^{(1)} - \sigma'_{0,1}^{(1)} = \frac{1}{2} \quad (7a.2)$$

$$\sigma_{0,1}^{(2)} + \sigma'_{0,1}^{(2)} = \frac{3}{4} \quad (7a.3)$$

$$\sigma_{0,1}^{(3)} - \sigma'_{0,1}^{(3)} = \frac{5}{2^4} \quad (7a.4)$$

$$\sigma_{0,1}^{(4)} + \sigma'_{0,1}^{(4)} = \frac{1}{2^2} \quad (7a.5)$$

$$\sigma_{0,1}^{(5)} - \sigma'_{0,1}^{(5)} = \frac{31}{3 \cdot 2^6} \quad (7a.6)$$

$$\sigma_{0,1}^{(6)} + \sigma'_{0,1}^{(6)} = \frac{89}{3 \cdot 2^8} \quad (7a.7)$$

$$\sigma_{0,1}^{(7)} - \sigma'_{0,1}^{(7)} = \frac{1467}{3^2 \cdot 2^{11}} \quad (7a.8)$$

Using the inequality (7.6), the smallest zero $g_{0,1}$ of $H_0(z)$ may be tabulated as follows :

TABLE I

z	$\left[\sigma_{0,1}^{(m)} + \sigma'_{0,1}^{(m)} \right]^{-1/m}$	$\frac{\sigma_{0,1}^{(m)} + \sigma'_{0,1}^{(m)}}{\sigma_{0,1}^{(m+1)} - \sigma'_{0,1}^{(m+1)}}$	Smallest zero of $H_0(z)$
2	1.155	3	
4	1.414	1.548	$g_{0,1} = 1.435$
6	1.432	1.456	

Determination of $h_{0,1}$

From the tables of Bessel functions, we get

TABLE II

z	$J_0(z)$	$J_1(z)$	$h_{0,1}$
3.10	- 0.2921	0.3009	
3.11	- 0.29503	0.2970	3.113
3.12	- 0.2980	0.2931	
3.113	- 0.2960	0.2958	

It is obvious from Tables I and II, that $h_{0,1} = 3.113$ satisfies the inequality (7.7) with the addition that $h_{0,1} > g_{0,1}$.

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On Double Orthogonal Series

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Abstract

In this paper I propose to prove the theorems for double orthogonal series corresponding to those theorems of A. Zygmund (9) for single orthogonal series.

1. Introduction

Let $\{\phi_{ij}(x, y)\}$ ($i, j = 1, 2, \dots$) be a sequence of orthonormal functions in the rectangle $R[a \leq x \leq b, c \leq y \leq d]$ i.e.

$$\iint_R \phi_{ij}(x, y) \phi_{kl}(x, y) dx dy = \begin{cases} 1 & \text{for } k = i, l = j \\ 0 & \text{for } k \neq i \text{ and } l \neq j. \end{cases}$$

Consider the double orthogonal series

$$(1.1) \quad \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} a_{ij} \phi_{ij}(x, y)$$

Where $\{a_{ij}\}$ is an arbitrary sequence of real numbers. The mn^{th} partial sums of (1.1) is given by

$$S_{mn}(x, y) = \sum_{k=1}^m \sum_{l=1}^n a_{kl} \phi_{kl}(x, y).$$

The series (1.1) is said to be $(c, 1, 1)$ summable to a function $s(x, y)$ if

$$\lim_{m, n \rightarrow \infty} \sigma_{mn}(x, y) = S(x, y).$$

$$\text{Where } \sigma_{mn}(x, y) = \sum_{k=1}^m \sum_{l=1}^n \left(1 - \frac{k-1}{m}\right) \left(1 - \frac{l-1}{n}\right) a_{kl} \phi_{kl}(x, y).$$

The convergence and Cesàro summability of single orthogonal series have been studied by Alexits⁽²⁾, Kaczmarz⁽⁴⁾, Menchoff⁽⁶⁾, Rademacher⁽⁷⁾, Tandori⁽⁸⁾ and Zygmund⁽⁹⁾, and those of the double orthogonal series by Agnew⁽¹⁾, Fedulov⁽³⁾ and Mitchell⁽⁵⁾.

In this paper I purpose to prove the following theorems :

Theorem 1. If

$$(1.2) \quad \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} a_{kl}^2 < \infty$$

then

$$\sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{mn(\log m \log n)^p} [S_{mn}(x, y) - \sigma_{mn}(x, y)]^2, \quad p > 1, \text{ is}$$

Convergent almost everywhere in R . ("means that the meaningless terms are omitted).

Theorem 2. If the series (1.1) is $(c, 1, 1)$ summable to a function $S(x, y)$ almost everywhere in R and the condition (1.2) is fulfilled then

$$\sum_{k=1}^m \sum_{l=1}^n \left(S_{kl}(x, y) - S(x, y) \right)^2 = O[mn(\log m \log n)^p], \quad p > 1,$$

as $m, n \rightarrow \infty$ almost everywhere in R .

2. Proof of Theorem 1. We have

$$\begin{aligned} S_{mn}(x, y) - \sigma_{mn}(x, y) &= \sum_{k=1}^m \sum_{l=1}^n a_{kl} \phi_{kl}(x, y) - \sum_{k=1}^m \sum_{l=1}^n \left(1 - \frac{k-1}{m}\right) \times \\ &\times \left(1 - \frac{l-1}{n}\right) a_{kl} \phi_{kl}(x, y) = \sum_{k=1}^m \sum_{l=1}^n a_{kl} \phi_{kl}(x, y) - \sum_{k=1}^m \sum_{l=1}^n a_{kl} \phi_{kl}(x, y) + \\ &+ \sum_{k=1}^m \sum_{l=1}^n \frac{(k-1)}{m} a_{kl} \phi_{kl}(x, y) + \sum_{k=1}^m \sum_{l=1}^n \frac{(l-1)}{n} a_{kl} \phi_{kl}(x, y) - \\ &- \sum_{k=1}^m \sum_{l=1}^n \frac{(k-1)(l-1)}{mn} a_{kl} \phi_{kl}(x, y) = \sum_{k=1}^m \sum_{l=1}^n \frac{(k-1)}{m} a_{kl} \phi_{kl}(x, y) + \\ &+ \sum_{k=1}^m \sum_{l=1}^n \frac{(l-1)}{n} a_{kl} \phi_{kl}(x, y) - \sum_{k=1}^m \sum_{l=1}^n \frac{(k-1)(l-1)}{mn} a_{kl} \phi_{kl}(x, y) \end{aligned}$$

By using the inequality $(a_1 + a_2 - a_3)^2 \leq 3(a_1^2 + a_2^2 + a_3^2)$ and the orthonormality property of the functions $(\phi_{mn}(x, y))$ we obtain

$$\begin{aligned} &\sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{mn(\log m \log n)^p} \iint_R \left[S_{mn}(x, y) - \sigma_{mn}(x, y) \right]^2 dx dy \leq \\ &\leq 3 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{mn} \sum_{k=1}^m \sum_{l=1}^n \frac{k^2 l^2 a_{kl}^2}{m^2 n^2} + \\ &+ 3 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{mn(\log n)^p} \sum_{k=1}^m \sum_{l=1}^n \frac{k^2 a_{kl}^2}{m^2} + \\ (2.1) \quad &+ 3 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{mn(\log m)^p} \sum_{k=1}^m \sum_{l=1}^n \frac{l^2 a_{kl}^2}{n^2} = \\ &= 3 \sum_1 + 3 \sum_2 + 3 \sum_3, \text{ say.} \end{aligned}$$

Let us consider the estimate with regard to Σ_1

$$\begin{aligned}
 \Sigma_1 &= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{m n} \sum_{k=1}^m \sum_{l=1}^n \frac{k^2 l^2 a^2_{kl}}{m^2 n^2} = \\
 &= \sum_{m=1}^{\infty} \frac{1}{m^3} \sum_{k=1}^m k^2 \sum_{n=1}^{\infty} \frac{1}{n^3} \sum_{l=1}^n l^2 a^2_{kl} = \\
 &= O(1) \sum_{k=1}^{\infty} k^2 \sum_{m=k}^{\infty} \frac{1}{m^3} \sum_{l=1}^{\infty} l^2 a^2_{kl} \sum_{n=l}^{\infty} \frac{1}{n^3} = \\
 (2.2) \quad &= O(1) \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} a^2_{kl} < \infty.
 \end{aligned}$$

Coming now to Σ_2 we get

$$\begin{aligned}
 \Sigma_2 &= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{mn (\log n)^p} \sum_{k=1}^m \sum_{l=1}^n \frac{k^2 a^2_{kl}}{m^2} = \\
 &= \sum_{m=1}^{\infty} \frac{1}{m^3} \sum_{k=1}^m k^2 \sum_{n=1}^{\infty} \frac{1}{n (\log n)^p} \sum_{l=1}^n a^2_{kl} = \\
 &= O(1) \sum_{k=1}^{\infty} k^2 \sum_{m=k}^{\infty} \frac{1}{m^3} \sum_{l=1}^{\infty} a^2_{kl} \sum_{n=1}^{\infty} \frac{1}{(n \log n)^p} = \\
 (2.3) \quad &= O(1) \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} a^2_{kl} < \infty, \text{ because } p > 1.
 \end{aligned}$$

Σ_3 can be dealt with in a similar manner. Combining (2.1), (2.2) and (2.3) our theorem is proved.

3. Proof of Theorem 2. We have

$$\begin{aligned}
 &\sum_{k=1}^m \sum_{l=1}^n (S_{kl}(x, y) - S(x, y))^2 \leq \\
 &\leq 2 \left\{ \sum_{k=1}^m \sum_{l=1}^n (S_{kl}(x, y) - \sigma_{kl}(x, y))^2 + \right. \\
 (3.1) \quad &\left. + \sum_{k=1}^m \sum_{l=1}^n (\sigma_{kl}(x, y) - S(x, y))^2 \right\}
 \end{aligned}$$

By the assumption

$$(3.2) \quad \sum_{k=1}^m \sum_{l=1}^n (\sigma_{kl}(x, y) - S(x, y))^2 = O(mn).$$

From theorem 1 and an extension of kronecker's theorem for simple series we get

$$\sum_{k=1}^m \sum_{l=1}^{n+1} \frac{1}{l (\log l)^p} (S_{kl} (x, y) - \sigma_{kl} (x, y))^2 = O (m) (\log m)^p.$$

From this follows that

$$(3.3) \quad \sum_{k=1}^m \sum_{l=1}^n (S_{kl} (x, y) - \sigma_{kl} (x, y))^2 = O (m n) (\log m \log n)^p.$$

Combining (3.1), (3.2) and (3.3) our theorem gets established.

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